Structural Investigations of the Organoantimony(V) Halides Ph_4SbX and Ph_3SbX_2 (X = Cl, Br or I) in the Solid State and in Solution†

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X-Ray crystallography revealed a distorted trigonal-bipyramidal structure for Ph_4SbI, with Sb–C_{ax} 2.141(3), Sb–C_{eq} 2.103(3)–2.117(3) Å and a long Sb–I distance of 3.341(1) Å in monoclinic crystals of $P2_1/n$ symmetry. Consideration of the weak Sb–X bonds in Ph_4SbX (X = Cl, Br or I) leads to reassignment of their Raman spectra; Ph_4SbI ionises forming $[Ph_4Sb]^+$ in acetonitrile, as shown by ^{13}C and ^{121}Sb NMR spectra. The halide Ph_3SbI_2 is reported in two phases, yellow, orthorhombic ($Fdd2$) crystals isomorphous with Ph_3SbBr_2 and off-white, cubic ($P4_332$) crystals. In each the molecule is trigonal-bipyramidal, with axial Sb–I bonds of 2.865(1) Å in the former and 2.885(1) Å in the latter, and small differences in their respective bond angles. The phenyl groups of the cubic form are in the regular propeller arrangement whereas one group of the orthorhombic form has a reversed orientation. The vibrational spectra of the two forms differ slightly.

Trigonal-bipyramidal molecular structures are common to many organoantimony(V) compounds, with the notable exception of Ph_5Sb which displays square-pyramidal symmetry in the crystalline state,[1] although it changes to trigonal-bipyramidal in the solvate $Ph_5Sb{\cdot}0.5C_6H_{12}$.[2] Ionic compounds such as $[Ph_4Sb]ClO_4$,[3] $[Ph_4Sb]I_3$[4] or $[Ph_3SbI]AsF_6$,[5] contain four-co-ordinate tetrahedral antimony species, while some antimony(V) molecules tend towards six-co-ordination.[6] Five-co-ordinate structures have been demonstrated for Ph_4SbCl[7] and Ph_4SbBr[3,8] by crystallographic study. Mössbauer spectroscopy clearly favours a molecular formulation for crystalline Ph_4SbI,[9] although the vibrational spectrum does not have a band in the expected 100–200 cm^{-1} range assignable to a Sb–I mode. Conductivity data for acetonitrile solutions indicate that the iodide exists as $[Ph_4Sb]^+I^-$, whereas Ph_4SbCl and Ph_4SbBr are little ionised.[9]

We have explored the structure of tetraphenylantimony iodide in comparison with the bromide by crystallographic and spectroscopic means. The triphenylantimony dihalides Ph_3SbX_2 (X = Cl, Br or I) for which five-co-ordinate molecular structures generally prevail were also examined. While this work was in progress an X-ray study of Ph_3SbI_2 was reported.[4] This species has been encountered again in the complex $[Ph_4Sb][FeI_4]{\cdot}Ph_3SbI_2$.[10] We report investigations into two crystal forms of Ph_3SbI_2, both molecular and free of trapped solvent, in which the structure deviates significantly from that already published.

Experimental

Tetraphenylantimony bromide was synthesised by the reaction of PhBr with Ph_3Sb and converted into Ph_4SbI **1** by crystallisation from aqueous KI solution.[11] Tetraphenylantimony tetrafluoroborate was prepared by treating Ph_4SbBr with $AgBF_4$ in acetonitrile, filtering to remove AgBr and evaporating to obtain crystals.

The dichloride, Ph_3SbCl_2, was prepared by the action of $SOCl_2$ upon Ph_3Sb[12] and recrystallised from ethanol. The dibromide, Ph_3SbBr_2, was obtained as colourless crystals which separated when Br_2 in diethyl ether was added dropwise to a solution of Ph_3Sb in the same solvent. The vibrational and ^{13}C NMR spectra of the Ph_3SbCl_2 and Ph_3SbBr_2 products exactly matched the literature data.[13–15]

The diiodide, Ph_3SbI_2, was made by combining equimolar quantities of Ph_3Sb and I_2 in dry dichloromethane, noting that the solution changed abruptly from yellow to brown if an excess of I_2 was added. Evaporation of the solvent in a desiccator yielded yellow flakes of Ph_3SbI_2 **2a**; the IR and Raman spectra of this compound agreed with the previously assigned values.[14] A different, almost colourless, crystalline form of Ph_3SbI_2 **2b** separated on combining Ph_3Sb with I_2 in dry diethyl ether and appeared unchanged after five days when the solvent phase was withdrawn and the crystals were collected. During this period a few dark brown crystals also formed. The infrared and Raman spectra of Ph_3SbI_2 in the off-white form **2b** differ slightly from those of the yellow form **2a** (see below). Recrystallisation of **2b** from CH_2Cl_2 gave a yellow material like that of the product **2a** already investigated.

Raman spectra of crystalline samples were observed using a Jobin Yvon U1000 spectrometer fitted with a microscope attachment. Excitation employed the green, 514 nm line of a Spex argon-ion laser operating at powers of 10–20 mW. Infrared spectra were recorded as mulls in petroleum jelly using Perkin-Elmer 983 or Digilab FTS60 instruments. Proton and ^{13}C NMR spectra of samples in deuteriated solvents were measured at 298 K with Bruker AC200 or AM400 spectrometers. Cross-polarisation magic angle spinning (CP MAS) ^{13}C NMR spectra of powdered crystalline samples were recorded at 75 MHz, using a spinning rate of 8000 Hz.

Single-crystal X-Ray Studies.—Recrystallisation of Ph_4SbI **1** from benzene gave colourless, cuboid crystals, one of which was mounted on a fibre. Yellow, tetrahedral crystals of Ph_3SbI_2 **2a** suitable for X-ray examination were obtained by recrystallising the flaky material from benzene; one of these was mounted. A crystal of the off-white form of Ph_3SbI_2 **2b** was taken for X-ray analysis directly from the reaction product.

The Enraf-Nonius CAD-4 diffractometer used graphite-monochromated Mo-Kα radiation, λ = 0.710 69 Å) and ω–2θ scans. Lorentz and polarisation corrections were applied using locally written programs and absorption corrections were applied from empirical psi scans.[16] The structures were solved

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Crystal data for the iodides **1**, **2a** and **2b**

		Ph_3SbI_2	
	Ph_4SbI **1**	**2a**	**2b**
Formula	$C_{24}H_{20}ISb$	$C_{18}H_{15}I_2Sb$	$C_{18}H_{15}I_2Sb$
Molecular weight	557.05	606.85	606.85
Crystal system	Monoclinic	Orthorhombic	Cubic
Space group	$P2_1/n$	$Fdd2$	$P4_332$
a/Å	12.630(3)	25.071(9)	12.365(3)
b/Å	10.588(1)	10.591(3)	
c/Å	16.542(3)	14.422(3)	
β/°	105.30(2)		
U/Å^3	2133.6(7)	3829(2)	1890.5(8)
Z	4	8	4
D_c/g cm^{-3}	1.734	2.105	2.132
$F(000)$	1072	2240	1120
μ/mm^{-1}	2.74	4.66	4.7
Crystal size/mm	0.40 × 0.35 × 0.3	0.33 × 0.33 × 0.25	0.30 × 0.25 × 0.18
T/K	293	293	291
2θ range/°	2–50	2–40	2–55
h, k, l range	$0 \leqslant h \leqslant 15$, $-12 \leqslant k \leqslant 0$, $-19 \leqslant l \leqslant 18$	$-24 \leqslant h \leqslant 0$, $0 \leqslant k \leqslant 10$, $0 \leqslant l \leqslant 13$	$0 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 6$, $0 \leqslant l \leqslant 16$
No. of unique reflections	3751	471	731
No. of observed reflections [$F > 4\sigma(F)$]	3225	455	577
$A_{\text{min, max}}$	1.00, 0.88	1.00, 0.69	1.00, 0.83
Least-squares weights P^a	0.023	0.091	0.024
Number of variables in least squares	236	98	34
Goodness of fit on F^2	1.086	1.118	1.087
R, $wR2$ [$I > 2\sigma(I)$]^b	0.021, 0.051	0.042, 0.103	0.0278, 0.0629
Maximum, minimum peak heights in final electron-density map/e Å^{-3}	0.44, −0.67	0.75, −0.86	0.25, −0.58

[a] Weighting scheme = $1.0/\{\sigma^2(F_o^2) + [P(F_o^2 + 2F_c^2)/3]^2\}$. [b] Function minimised, $\Sigma w[F_o^2 - F_c^2]^2$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

Table 2 Atomic coordinates (× 10^4) for Ph_4SbI **1**

Atom	x	y	z
I	1272(1)	1838(1)	1496(1)
Sb	2389(1)	1729(1)	−122(1)
C(11)	2476(2)	−179(3)	243(2)
C(12)	1716(3)	−1043(3)	−187(2)
C(13)	1849(4)	−2298(4)	18(3)
C(14)	2734(4)	−2690(4)	630(3)
C(15)	3487(4)	−1847(4)	1060(3)
C(16)	3361(3)	−574(3)	870(2)
C(21)	3675(2)	2873(3)	592(2)
C(22)	3540(3)	3749(3)	1171(2)
C(23)	4426(3)	4459(3)	1608(2)
C(24)	5445(4)	4264(4)	1487(3)
C(25)	5577(3)	3388(5)	912(3)
C(26)	4699(3)	2694(4)	460(3)
C(31)	921(2)	2661(3)	−723(2)
C(32)	810(3)	3930(3)	−605(2)
C(33)	−101(3)	4566(4)	−1081(3)
C(34)	−883(3)	3944(5)	−1659(2)
C(35)	−779(4)	2687(5)	−1770(3)
C(36)	121(3)	2026(4)	−1302(3)
C(41)	2970(2)	1512(3)	−1218(2)
C(42)	3401(3)	385(3)	−1417(2)
C(43)	3773(3)	305(4)	−2133(2)
C(44)	3720(3)	1328(4)	−2643(2)
C(45)	3303(3)	2451(4)	−2450(2)
C(46)	2921(3)	2538(4)	−1749(2)

Table 3 Atomic coordinates (× 10^4) for Ph_3SbI_2 **2a**

Atom	x	y	z
Sb	0	0	−12(1)
I(1)	−482(1)	2451(1)	44(1)
C(1)	668(8)	697(16)	−795(10)
C(2)	1169(8)	472(26)	−460(18)
C(3)	1590(8)	975(35)	−1023(23)
C(4)	1489(11)	1571(27)	−1845(23)
C(5)	996(14)	1723(31)	−2097(20)
C(6)	580(10)	1331(23)	−1555(19)
C(11)	0	0	1467(15)
C(12)	453(11)	−16(23)	1909(16)
C(13)	422(11)	257(31)	2865(18)
C(14)	0	0	3373(22)

Table 4 Atomic coordinates (× 10^4) for Ph_3SbI_2 **2b**

Atom	x	y	z
Sb	3 750	1 250	8 750
I(1)	5 097(1)	−97(1)	10 097(1)
C(1)	2 535(3)	35(3)	8 750
C(2)	2 088(5)	−319(4)	7 797(4)
C(3)	1 300(6)	−1 109(4)	7 804(5)
C(4)	961(4)	−1 539(4)	8 750

from Patterson and heavy-atom electron-density syntheses and refined by full-matrix least squares on F^2.[17] Flack's x parameter[18] for establishing absolute configuration was 0.09(16) for **2a** and 0.07(13) for **2b**. All atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and allowed to ride on atoms to which they are attached with 20% greater thermal parameter.

For Ph_3SbI_2 **2b**, the absolute structure parameter[19] indicates that the correct space group is $P4_332$ rather than the enantiomeric $P4_132$. The antimony atom of **2b** lies on the 8*b* special position so that the molecule has crystallographically required D_3 symmetry. Crystal data for the iodides **1**, **2a** and **2b** are given in Table 1, together with details of the data collection and refinement. Tables 2–4 contain the final refined atomic coordinates.

Additional material available from the Cambridge Crystallo-

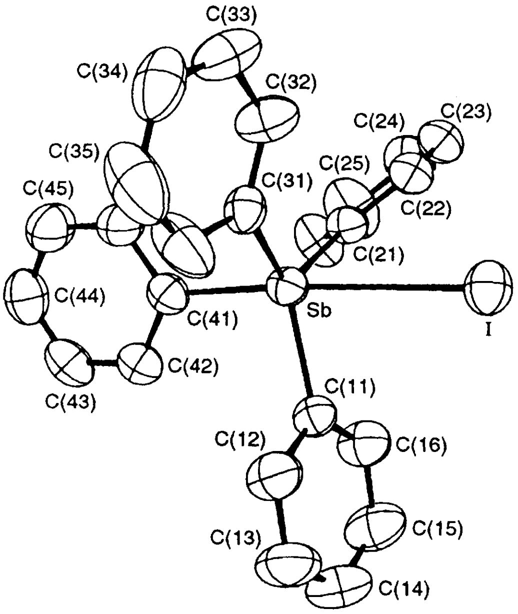

Fig. 1 The Ph_4SbI molecule with 50% thermal ellipsoids

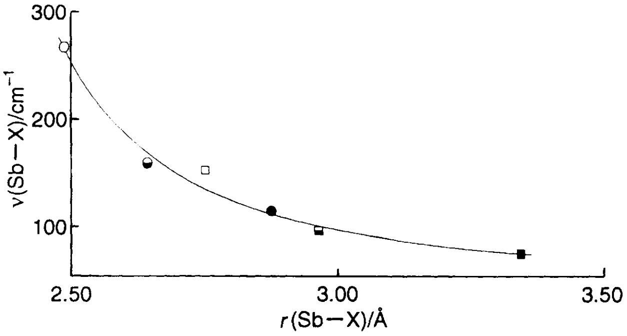

Fig. 2 Relationship between $\nu(Sb–X)_{sym}$ and the Sb–X bond distance in phenylantimony halides; Ph_3SbCl_2 ○, Ph_3SbBr_2 ⊖, Ph_3SbI_2 ●, Ph_4SbCl □, Ph_4SbBr ⬓, Ph_4SbI ■

Table 5 Selected bond distances (Å) and angles (°) for Ph_4SbI **1**

Sb–I	3.3413(7)	Sb–C(31)	2.105(5)
Sb–C(11)	2.103(3)	Sb–C(41)	2.141(3)
Sb–C(21)	2.117(3)		
C(41)–Sb–I	173.77(8)	I–Sb–C(21)	87.58(9)
C(41)–Sb–C(11)	97.85(12)	I–Sb–C(31)	81.74(8)
C(41)–Sb–C(21)	98.60(12)	C(11)–Sb–C(21)	114.54(11)
C(41)–Sb–C(31)	96.10(11)	C(11)–Sb–C(31)	123.99(12)
I–Sb–C(11)	78.72(8)	C(21)–Sb–C(31)	116.44(12)

graphic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Tetraphenylantimony Halides.—The structure of Ph_4SbI consists of discrete five-co-ordinate molecules having a distorted trigonal-bipyramidal framework; see Fig. 1. Iodine, in an axial position, makes a C_{ax}–Sb–I angle of 173.8° (Table 5) with the antimony atom, while the three equatorial phenyl groups are displaced towards the iodine giving a mean C_{ax}–Sb–C_{eq} angle of 97.5°. The Sb–C_{ax} bond, 2.141(3) Å, is slightly longer than the Sb–C_{eq} bonds which average 2.108 Å. A remarkable feature of the structure is the long Sb–I bond of 3.3413(7) Å. This is 20% greater than the sum of the covalent radii (2.73 Å)[20] and almost half-way to the van der Waal's distance of 4.03 Å. Bridging bonds of 3.4 Å occur in $[Ph_2Sb_2I_6]^{2-}$ and $[Ph_2Sb_2I_7]^{3-}$,[21] however a terminal Sb–I bond greater than 3.0 Å is without precedent.

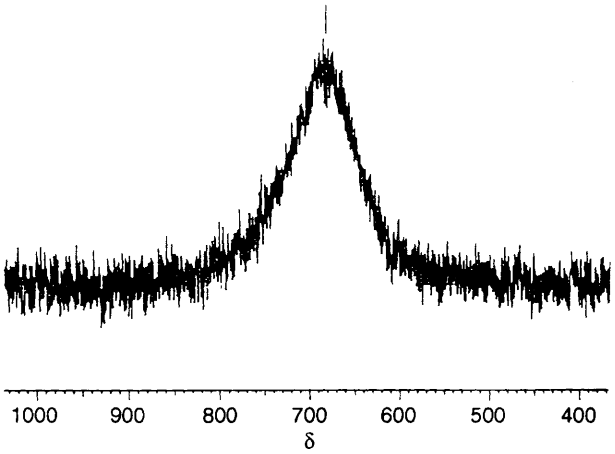

Fig. 3 Antimony-121 NMR spectrum of Ph_4SbI in CD_3CN recorded at 95.755 MHz

The structure of Ph_4SbI confirms the trend to long antimony–halide bonds in Ph_4SbCl (Sb–Cl 2.74 Å)[7] and Ph_4SbBr (Sb–Br 2.96 Å).[3,8] Recognising that such bonds should be weak, the vibrational spectra of the Ph_4SbX series were re-examined. Apart from lattice modes, most bands are due to phenyl modes and are little affected by the nature of X. However there are strong Raman features at 60 cm^{-1} (X = I) and 96 cm^{-1} (X = Br) which can be associated with stretching of the Sb–X bonds. The chloride Ph_4SbCl has a corresponding band[22] at 156 cm^{-1} which may be similarly assigned to the ν(Sb–Cl) mode. In support of these assignments, Fig. 2 shows that these values, and those of $\nu(Sb–X)_{sym}$ of Ph_3SbX_2, give a smooth curve when plotted against the Sb–X bond length. The earlier assignments[22] of Sb–X stretching modes at 263 cm^{-1} for Ph_4SbBr and 353 cm^{-1} for Ph_4SbCl now appear untenable. The detection of this Raman band is a sure sign of covalent bonding. Without this spectroscopic evidence a case could be made for the ionic structure, especially for the iodide, although to explain the unusual shape of the $[Ph_4Sb]^+$ moiety would then present a problem.

For structural information on tetraphenylantimony iodide in solution we turned to NMR spectroscopy, using ^1H, ^{13}C and ^{121}Sb techniques. The ^1H and ^{13}C NMR spectra support the presence of $[Ph_4Sb]^+$ when Ph_4SbI is dissolved in acetonitrile, and are like those of $[Ph_4Sb]BF_4$. Sharp ^{13}C NMR signals belonging to the phenyl groups are observed at δ 130.0 (C_{meta}), 132.7 (C_{para}) and 134.6 (C_{ortho}). The upfield location of the C_{ipso} signal, δ 121.6, indicates a shielded environment for this carbon and is in harmony with data for $[Ph_4As]^+$ and $[Ph_4P]^+$.[23] The quadrupolar ^{121}Sb nucleus permits NMR detection only in situations of high symmetry.[24] As shown in Fig. 3, the solution of Ph_4SbI in CD_3CN displays a strong, broad resonance, δ 685, $w_{\frac{1}{2}}$ = 9000 Hz (relative to $SbCl_6^-$). This is a credible value for the $[Ph_4Sb]^+$ ion, being rather more shielded than that of $[Me_4Sb]^+$, δ 780.[25] Only a very broad, low intensity ^{121}Sb resonance could be obtained from Ph_4SbBr in CD_3CN.

The ^{13}C NMR signals of Ph_4SbBr show a marked dependence on the temperature and concentration as well as the nature of the solvent (CD_3CN, $CDCl_3$ or C_6H_6) which directs attention to probable changes in the structure. However the pattern never attains that corresponding to $[Ph_4Sb]^+$. In the non-polar solvent benzene, the spectrum probably belongs to the Ph_4SbBr molecule and is closely similar to that of Ph_3SbBr_2,[15] which appears in Fig. 5, below. The ^{13}C chemical shifts of Ph_4SbBr and Ph_3SbBr_2 measured as solids by CP MAS

Table 6 Selected bond distances (Å) and angles (°) for Ph_3SbI_2

Orthorhombic form **2a**

Sb–I(1)	2.865(1)	Sb–C(11)	2.13(2)
Sb–C(1)	2.15(2)		
I(1)–Sb–I(1′)	176.8(1)	C(1)–Sb–C(1′)	116.6(8)
I(1)–Sb–C(1)	91.9(5)	Sb–C(1)–C(2)	118(1)
I(1)–Sb–C(1′)	89.8(5)	Sb–C(1)–C(6)	119(2)
I(1)–Sb–C(11)	88.4(1)	Sb–C(11)–C(12)	119(1)
C(1)–Sb–C(11)	121.7(4)		

Torsion angle of phenyl groups with respect to I(1): 53.1, 53.1, −65.4

Cubic form **2b**

Sb–I(1)	2.885(1)	Sb–C(1)	2.125(6)
I(1)–Sb–I(1′)	180.0	C(1)–Sb–C(1′)	120.0
I(1)–Sb–C(1)	90.0	Sb–C(1)–C(2)	120.7(3)

Torsion angle of phenyl groups with respect to I(1): 50.8

NMR spectroscopy are near the benzene solution values. Five-co-ordinate molecular structures for both of these bromides in the crystalline state have been firmly established by X-ray[3,8,16] and Raman investigations.[13,14,22]

Triphenylantimony Dihalides.—The diiodide, Ph_3SbI_2, is formed as a yellow product upon addition of I_2 to Ph_3Sb and easily recognised by its known ^{13}C NMR spectrum,[15] although if moisture is present $(Ph_3SbI)_2O$ is liable to be produced.[26,27] The yellow crystals of Ph_3SbI_2, **2a**, have an orthorhombic unit cell of *Fdd*2 symmetry and are composed of discrete five-co-ordinate molecules whose geometry is close to trigonal bipyramidal, see Table 6. The I–Sb–I angle is 176.8(1)° and the Sb–I bonds are equal at 2.865(1) Å. The Sb–C bonds are in the range 2.13(2)–2.15(2) Å. The diiodide **2a** is isostructural with Ph_3SbBr_2, depicted elsewhere,[28] and has a two-fold axis passing through the Sb atom and the C(11) and C(14) atoms of one of the phenyl groups. It has a similar arrangement of the phenyl rings, one of which has a reversed orientation.

Triphenylantimony diiodide has been reported in a different form, of which the symmetry is triclinic.[4] This crystal has two independent molecules in the unit cell; one with Sb–I 2.875(3) Å subtending an angle of 172.7(1)°, and another with Sb–I bonds of 2.853(2) and 2.903(2) Å and an angle of 168.1°. The distortion arouses interest because it suggests rearrangement of the trigonal-bipyramidal structure towards a rectangular pyramid. A hint that Ph_3SbI_2 might exist in more that one crystalline form appears in earlier preparative work where colourless and yellow products are mentioned,[26] and the ease with which organoantimony(v) systems undergo structural change draws frequent comment.[29]

We have prepared Ph_3SbI_2 in the solvents MeCN, $CHCl_3$, CH_2Cl_2 and benzene, all of which appear to give the yellow product described above. When the reaction of Ph_3Sb with I_2 was conducted in dry Et_2O it yielded off-white crystals which we assumed to be those of the solid obtained by the previous workers.[4] A specimen was mounted in order to confirm its identity by unit-cell measurement. To our surprise the crystal was of a different space group (cubic $P4_332$), and therefore we proceeded to solve the structure. It presents yet another modification of the Ph_3SbI_2 molecule. This time the co-ordination around antimony forms a perfectly regular trigonal bipyramid with bond angles of 90 or 120°. In **2b** the iodine atoms occupy the axial sites, with Sb–I 2.885(1) Å. The Sb–C distance is 2.125(6) Å. In contrast to **2a**, the phenyl groups are uniformly twisted by 39° out of the equatorial plane to give a regular propeller arrangement.

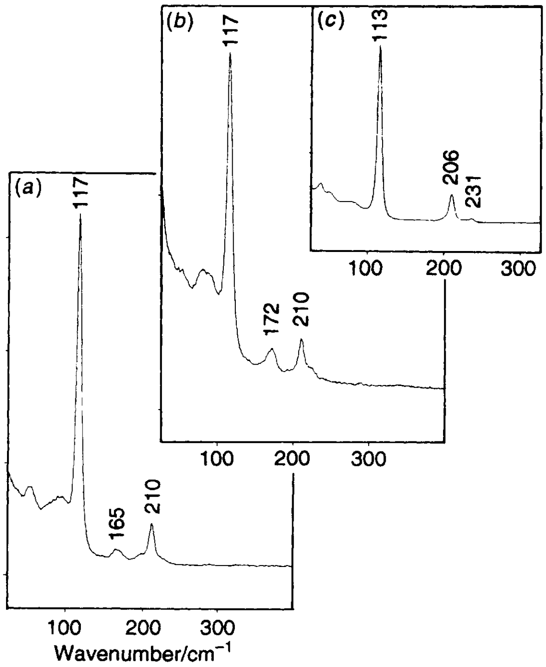

Fig. 4 Raman spectra of Ph_3SbI_2; bulk sample (*a*) and mounted crystal (*b*) of the yellow form, (*c*) mounted crystal of the off-white form

The two crystalline forms of triphenylantimony diiodide reported here and the solids described elsewhere[4,10] encompass five versions of the Ph_3SbI_2 molecule. In these species the I–Sb–I angle ranges from 168 to 180°. The Sb–I bond lengths range from 2.85 to 2.91 Å, averaging 2.877 Å, and the Sb–C distances from 2.04 to 2.15 Å, without any obvious pattern. The structures are similar and yet the differences are significant. Five-co-ordinated structures are well known to be conformationally labile. Hence the trapping of a particular variant from solution during the nucleation of a crystalline solid phase seems to be at the heart of the phenomenon. The fact that two different crystals of Ph_3SbI_2 have been obtained from the reaction of Ph_3Sb with I_2 in diethyl ether, apparently under the same experimental conditions, is more difficult to explain. The product of McAuliffe and co-workers[4] apparently gives a Raman band at 111 cm^{-1}, assigned to ν(Sb–I), and the spectrum in that report also has a strong band at *ca.* 175 cm^{-1} which could indicate the presence of $[Ph_3SbI]^+$.[5] Our product does not exhibit this latter feature.

To characterise the present materials as closely as possible, we used Raman microscopy to record the spectrum of each of the Ph_3SbI_2 crystals, **2a** and **2b**, on the X-ray mount after collecting the diffraction data. These spectra, one of which has $\nu(Sb–I)_{sym}$ at 117 cm^{-1} and the other at 113 cm^{-1}, are shown in Fig. 4, where they are compared with the spectrum of a bulk sample of Ph_3SbI_2. The IR spectra of orthorhombic (yellow) and cubic (off-white) forms of Ph_3SbI_2 were carefully examined by overlaying the two spectra. These are very similar, although differing by up to 5 cm^{-1} in the positions of some of the principal bands. The orthorhombic form shows additional weak or very weak bands, and this is certainly the solid Ph_3SbI_2 whose spectrum is reported in the literature.[14]

The ^{13}C NMR spectra of the Ph_3SbX_2 molecules (X = Cl, Br or I), previously observed in $CDCl_3$,[15] differ little in CD_2Cl_2, CD_3CN or benzene. Mixtures, *e.g.* Ph_3SbBr_2 and Ph_3SbI_2, produce Ph_3SbBrI. As shown in Fig. 5, the ^{13}C NMR resonances now appear as groups of three signals in the ratio 1 : 2 : 1, demonstrating that halide exchange is facile, but slow on the NMR timescale, since the individual spectrum of each of these triphenylantimony dihalides is clearly seen. Like other antimony(v) species, the Ph_3SbX_2 molecules will possess a

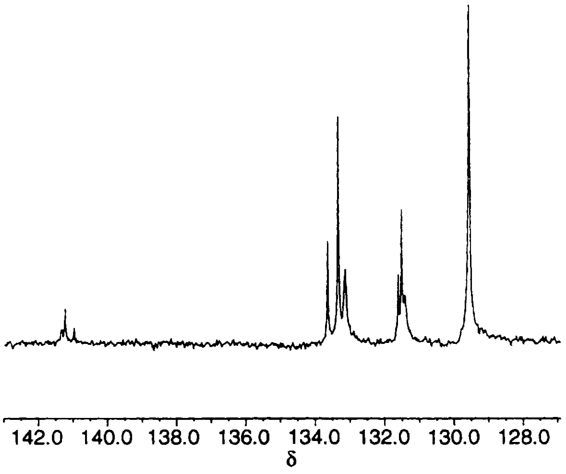

Fig. 5 Carbon-13 NMR spectra of Ph_3SbBr_2 and Ph_3SbI_2 in $CDCl_3$ at 25 °C showing the formation of Ph_3SbBrI (largest peaks) with δ 141.2 (C_{ipso}), 133.35 (C_{ortho}), 131.5 (C_{para}) and 129.5 (C_{meta})

low barrier to conformational change. This property is a characteristic of both Ph_4SbBr, studied here, and Ph_5Sb[30] whose NMR spectra fail to distinguish between axial and equatorial phenyl groups even at low temperatures.

Dark brown crystals which formed as a by-product during the reaction of Ph_3Sb with I_2 in diethyl ether to give **2b** were shown by X-ray investigation to be $[Ph_4Sb]I_3$ of monoclinic space group *P*2/*n* with unit-cell dimensions matching the known values.[4] Similar interconversion of Ph_3SbI_2 has been observed previously in acetonitrile.[4] Tetraphenylantimony triiodide has ionic character and crystallises as $[Ph_4Sb]^+I_3^-$, although Ph_4SbI (like Ph_3SbI_2) is a molecular solid.

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