The Shape of Pentaphenylantimony and Pentaphenylarsenic in Solution

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From a detailed study of the vibrational spectra of pentaphenylantimony and pentaphenylarsenic it is suggested that the compounds are respectively square pyramidal and trigonal bipyramidal in solution. ^{13}C Resonance spectroscopy on solutions of pentaphenylantimony at room temperature show the phenyl rings to be magnetically equivalent. Proton magnetic resonance on solutions of pentaphenylantimony which had been fully deuteriated in the *meta* and *para* positions showed only one line, which broadened as the temperature was lowered to −140°.

PENTAPHENYLANTIMONY is unique in that it is a covalent compound of a non-transition element, containing no ' lone pair ' electrons but with an approximately square pyramidal shape for the SbC_5 skeleton.[1] The only other well established example of this behaviour for the non-transition elements occurs in the ion $InCl_5^{2-}$ in the compound $(Et_4N)_2InCl_5$.[2] The $InCl_5^{2-}$ ion in this case has rigorously C_{4v} symmetry, in sharp contrast to the trigonal-bipyramidal configuration of the isoelectronic species $SnCl_5^-$ and $SbCl_5$. Although in the solid state both pentaphenylphosphorus [3] and pentaphenylarsenic [3] have approximately trigonal-bipyramidal MC_5 skeletons, the square-pyramidal SbC_5 skeleton of the antimony compound (found by *X*-ray structural investigation) could be due to packing in the solid state. The shape of this molecule in solution is therefore of considerable interest. The two most valuable techniques for such a study are n.m.r. spectroscopy and vibrational spectroscopy.

Vibrational Spectroscopy.—The assignment of the structure of pentaphenylantimony in solution from vibrational spectroscopy is a formidable task. The procedure adopted was to obtain solution and solid-state i.r. and Raman data (including detailed polarisation measurements) for both pentaphenylantimony and pentaphenylarsenic. The vibrational spectra were then computed from force constants transferred from tetramethylgermanium,[4] tetramethyltin,[4] and pentamethylantimony.[5]

In Tables 1 and 2 the spectra of pentaphenylantimony and pentaphenylarsenic in the solid state and in solution in dichloromethane and dibromomethane are recorded for the region below 400 cm^{-1}. Inspection of these tables shows that the spectra in solution closely resemble those obtained in the solid state. None of the differences observed is so great that it could not be attributed to a change of state without change in molecular shape. Initial calculations based on the molecular shapes found from *X*-ray structural investigations demonstrated (not unexpectedly) that for such complicated molecules the number of bands predicted in a small frequency range is so large that assignment on the basis of either square-pyramidal or trigonal-bipyramidal symmetry would be acceptable. The problem lies in the inability to predict intensities. If the phenyl rings are now considered to be freely rotating the symmetries can be allowed to rise from C_{2v} to C_{4v} (square pyramidal) or from C_{2v} to D_{3h} (trigonal bipyramidal). The assignments for penta-

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[1] P. J. Wheatley, *J. Chem. Soc.*, 1964, 3718; A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Amer. Chem. Soc.*, 1968, **90**, 6675.

[2] D. S. Brown, F. W. B. Einstein, and D. G. Tuck, *Inorg. Chem.*, 1969, **8**, 14 and references therein.

[3] P. J. Wheatley, *J. Chem. Soc.*, 1964, 2206.

[4] E. R. Lippincott and M. C. Tobin, *J. Amer. Chem. Soc.*, 1952, **75**, 4141.

[5] R. R. Holmes, R. M. Deiters, and J. A. Golez, *Inorg. Chem.*, 1969, **8**, 2612.

phenylantimony and pentaphenylarsenic on this basis are shown in Tables 3 and 4.*

TABLE 1

Vibrational spectrum of pentaphenylantimony below 400 cm^{-1} (cm^{-1})

Solid		Saturated solution in CH_2Cl_2 or CH_2Br_2	
Raman	I.r.	Raman	I.r.
284mw		282mw, ρ = 0·61	283s
	276vs	262w	262s
262mw	265vs	243vvw	
244w	245wsh		225wsh
224wsh	228mw	208vs, ρ *ca.* 0·1	
	215mw		200wsh
207vs	208w	165m, ρ *ca.* 0·75	164w
193w			
180mw			
161ms	164m		
137mw			
87s			
81msh			
	74w		
55w			
	40vw		

TABLE 2

Vibrational spectrum of pentaphenylarsenic below 400 cm^{-1} (cm^{-1})

Solid		Saturated solution in CH_2Cl_2 or CH_2Br_2	
Raman	I.r.	Raman	I.r.
350mw	354vs	351mw, ρ *ca.* 0·75	355vs
295w	296vs		294vs
260m	260m	263m	262mw
238mw	244m	240mw	241mw
	227m		229mw
221vs	216w	221vs, ρ *ca.* 0·1	
203m	204w		210w
175s	178mw		206vw
99m		178wsh	180vw
81s		164m, ρ ca. 0·5	

TABLE 3

Calculated (D_{3h} and C_{4v}) and observed frequencies for pentaphenylantimony †

D_{3h}			Observed		C_{4v}		
A_1	189	ν Sb–C eq.	208	282	A_1	270	ν Sb–C ax.
	165	ν Sb–C ax.	165	208		194	ν Sb–C bas.
						154	δ Sb–Ph
A_2'	248	ν Sb–C ax.	262			58	δ Sb–C o.p.
	185	ρν Sb–C and ν Sb–C ax.			A_2	170	v. mixed
	47	δ Sb–C o.p.				33	v. mixed
					B_1	144	ρ Sb–Ph
E	267	ν Sb–C eq.	282	165	B_2	188	ν Sb–C bas.
	147	ρν Sb–C i.p.				124	δ Sb–Ph
	130	ρν Sb–Ph and δ Sb–C o.p.				21	δ Sb–Ph o.p.
	42	ρν Sb–Ph and δ Sb–Ph		262	E	290	ν Sb–C bas.
	20	δ Sb–C o.p.				167	ρ Sb–Ph and δ Sb–C
						145	
E	163	δ Sb–C o.p.				81	δ Sb–Ph o.p. and δ Sb–Ph i.p.
	122	ρν Sb–Ph				43	
	32	v. mixed				23	

† Force constants from tetramethyltin.

TABLE 4

Calculated (D_{3h} and C_{4v}) and observed frequencies for pentaphenylarsenic

D_{3h}			Observed		C_{4v}		
A_1	206	ν As–C eq.	221	351	A_1	340	ν As–C ap.
	180	ν As–C ax.	164	221		210	ν As–C bas.
						170	δ As–C
A_2''	312	ν As–C ax.	294			62	δ As–Ph
	199	ρν As–Ph and δ As–Ph			A_2	170	mixed defs.
	57	δ As–C and ρν As–Ph				33	mixed δ and ρ
					B_1	144	ρ As–Ph
E'	337	ν As–C eq.	351	164 or 210	B_2	203	ν As–C
	165	δ As–C i.p.				137	δ As–C
	130	ρ As–Ph and δ As–Ph				21	δ As–Ph
	47	ρ As–Ph and δ As–Ph		294?	E	363	ν As–C bas.
	23	δ As–C o.p.				172	ρ As–Ph and δ As–C
E''	175	δ As–C o.p.				151	
	124	ρ As–Ph				84	very mixed δ and ρ
	37	δ As–Ph o.p.				44	
						23	

A possible means of distinction between the two molecular shapes is *via* polarisation measurements in the Raman effect. Predicted A_1 skeletal modes and assigned A_1 fundamentals in the region below 400 cm^{-1} are (cm^{-1}):

$SbPh_5$						
Calc.	D_{3h}			189	165	
Obs.			282	208		
Calc.	C_{4v}		270	194	154	58
$AsPh_5$						
Calc.	D_{3h}		206	180		
Obs.			221	164		
Calc.	C_{4v}	340	210	170	62	

The band at 208 cm^{-1} in pentaphenylantimony is strongly polarised, whereas that at 282 cm^{-1} has a ρ_P value of only 0·61, compared with 0·75 for a depolarised band. The medium intensity band at 165 cm^{-1} is not measurably polarised. For pentaphenylarsenic the band at 221 cm^{-1} is strongly polarised while the 164 cm^{-1} band has a ρ_P value of 0·55. By contrast with pentaphenylantimony the band of the highest frequency in the region studied is not measurably polarised.

Although these results cannot be considered to be unambiguous, the close similarity of the solution and solid-state spectra coupled with the excellent agreement between calculation and observation for (polarised) a_1 modes suggests the solid-state configuration is essentially retained in solution.

N.m.r. Spectroscopy.—N.m.r. spectroscopy on a species such as pentaphenylantimony is complicated by two factors, the complexity of the spectrum (for protons) due to the presence of a large number of nuclei of similar chemical shift (leading to second-order spectra) and the fluxional nature of the whole molecule (leading to apparent equivalence of magnetically non-equivalent nuclei). We therefore adopted two approaches, the observation of ^{13}C (natural abundance) spectra on pentaphenylantimony and the observation of proton spectra (at low temperature) for pentaphenylantimony where all protons except those *ortho* to the antimony had been deuteriated. The ^{13}C spectra (proton-noise decoupled)

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* Where a degenerate mode in higher symmetry correlates with two non-degenerate modes in the lower symmetry the mean of the two calculated non-degenerate frequencies is given.

at room temperature showed three sharp lines, indicating that the rings were effectively magnetically equivalent. On the basis of intensity and by comparison with the spectrum of triphenylantimony the lines were assigned to *ortho* (58·4), *para* (65·1), and *meta* (65·5) carbon atoms.* The resonance of the carbon directly attached to antimony was not observed presumably because of the lack of an Overhauser effect, coupled with quadrupole broadening by the antimony.

Proton n.m.r. spectra of the compound fully deuteriated in the *meta* and *para* positions of the phenyl rings showed only a single line down to $-142°$, although below $-100°$ broadening and some asymmetry appeared. The broadening was apparently not due to viscosity effects as the ethyl bromide quartet did not show similar signs of broadening.†

EXPERIMENTAL

Pentaphenylantimony and pentaphenylarsenic were prepared by literature methods[1,6,7] and recrystallised respectively from acetonitrile and cyclohexane after treatment of the solutions with activated charcoal. The solids were pumped dry under high vacuum.

Solutions for i.r. and Raman spectroscopy were made up in dichloromethane and in dibromomethane, in each case being treated with activated charcoal before filtration into the cell. The i.r. spectra of the solutions were studied in cells made of flattened Polythene tubing, using a Beckman IR 11. Similarly Nujol mulls were studied between Polythene plates. Solid-state Raman spectra were obtained using a Cary 81 with He–Ne laser excitation. Solutions were studied in capillary tubes using both a Cary 81 Raman spectrometer with He–Ne excitation and a 1401 Spex monochromator with Ar^+ laser excitation.

For the n.m.r. experiments carried out on an HA 100 Varian spectrometer the preparation of 3,4,5-trideuteriobromobenzene was necessary:‡ *p*-bromoanilinium chloride (20·7 g) was treated with deuterium oxide at 100° for 24 h.[8] Volatile material was then removed at *ca.* 50° whilst the mixture was stirred; more deuterium oxide was then added and the system was again heated at 100° for 24 h. This procedure was repeated to give a total of five treatments, with a total of 100 ml of deuterium oxide being added. The resulting suspension of 4-bromo[2,6-$^2H_2$]anilinium chloride was treated with deuterium oxide (40 ml) and deuterium chloride solution (15 ml, obtained by the hydrolysis of 7·2 g of silicon tetrachloride with the calculated quantity of deuterium oxide, the resultant DCl being absorbed in deuterium oxide). The whole was then cooled to 3° and a solution of sodium nitrite (7 g) in deuterium oxide (15 ml) was added dropwise with stirring. After completion of the diazotisation the practically clear solution was added gradually with stirring, the reaction temperature being kept below 7°, to a solution of freshly precipitated hydrated (D_2O) tin oxide in sodium deuterioxide solution.[9] [This solution was obtained by treating anhydrous tin dichloride (40 g) with deuterium oxide (140 ml) until a milky solution was obtained. A solution of sodium deuterioxide § (50 g) in deuterium oxide (130 ml) was then added, the temperature being kept below 20°.] The solution was allowed to warm to room temperature, and after a further hour was steam distilled. The yellow brown oil was separated from the aqueous phase, the aqueous phase was extracted with ether and, after being dried ($CaCl_2$) was fractionated; the fraction b.p. 150—154° was collected. Yields were low, *ca.* 10%, due in part to the extreme sensitivity of the alkaline tin(II) solutions to oxygen.

APPENDIX

In the case of the calculations on pentaphenylantimony, force constants were transferred either from pentamethylantimony or from tetramethyltin. For the pentaphenylarsenic calculations a scaling factor was introduced for the transference scheme from pentamethylantimony, *i.e.* $f(Me_5Sb) \times f[(Me_4Ge)/f(Me_4Sn)]$. Alternatively a direct transfer from tetramethylgermanium was used. The force constants for the phenyl residues were obtained from those calculated for benzene.[10]

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* Shifts recorded as p.p.m. from carbon disulphide, spectra at 25·15 MHz.

† The solvent used was 45% light petroleum (b.p. 30—40), 45% ethyl bromide, and 10% trichlorofluoromethane.

‡ This method of preparation was suggested by Dr. J. Hudec.

§ Obtained from the solution of disodium monoxide in deuterium oxide, the disodium monoxide having been obtained from the reaction of sodium with sodium hydroxide.

[6] See for example D. M. Adams and J. B. Raynor, 'Advanced Practical Inorganic Chemistry,' Wiley, London, 1965; H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Amer. Chem. Soc.*, 1933, **55**, 1252.

[7] G. Wittig and K. Clauss, *Annalen*, 1952, **577**, 26.

[8] A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 1946, 239.

[9] See for example N. Kornblum, *Org. Reactions*, 1944, **2**, 262.

[10] See D. A. Long, F. S. Murfin, and E. L. Thomas, *Trans. Faraday Soc.*, 1963, **59**, 12.