

## A reinvestigation of the vibrational spectroscopy of pentaphenylarsenic and pentaphenylantimony

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**Abstract**—The laser-Raman and infrared spectra of pentaphenylarsenic and pentaphenylantimony have been recorded both in the solid state and in solution. Structural conclusions for these molecules are based on an analysis of the phenyl-metal vibrations. These show that both pentaphenylarsenic and pentaphenylantimony retain their solid state geometries, trigonal bipyramidal and square pyramidal respectively, in solution.

### INTRODUCTION

THE STRUCTURE of pentaphenylantimony is unique among the pentaphenyl derivatives of the group V metals in that it forms a square pyramid in the solid state [1, 2]. In contrast, both pentaphenylphosphorus [3] and pentaphenylarsenic [3] have been shown to be trigonal bipyramidal by X-ray diffraction studies. Recent studies on the vibrational spectroscopy of pentacyclopropyl antimony [4] show it to have a square pyramidal skeleton in carbon disulfide solution. Pentamethylantimony on the other hand is trigonal bipyramidal as a neat liquid [5]. It has been suggested that the unusual geometry of pentaphenylantimony is due to crystal packing factors [5, 6]. To eliminate the solid state interactions it is necessary to study this molecule in the solution phase.

Structural studies of molecules of the  $ML_5$  type by nuclear magnetic resonance is unsatisfactory because of the long time scale of the measurements. All previous NMR studies on  $ML_5$  molecules have indicated magnetic equivalence of the ligand nuclei [7]. Pentaphenylantimony, [8] penta-*p*-tolyl-antimony, [9] and pentamethylantimony [10] have all been investigated by NMR without any definitive results regarding the geometry of these molecules. The most promising method to study these molecules is vibrational spectroscopy. MAC KAY, SOWERBY and YOUNG

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- [5] A. J. DOWNS, R. SCHMUTZLER, and I. A. STEER, *Chem. Comm.* 221 (1966).
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- [9] D. HELLWINKEL, *Angew. Chem.* **78**, 749 (1966).
- [10] E. L. MUETTERTIES, W. MAHLER, K. J. PACKER and R. SCHMUTZLER, *Inorg. Chem.* **3**, 1298 (1964).

[11] reported the infrared spectrum of pentaphenylarsenic and pentaphenylantimony in the solid state, but did not examine these molecules in solution. During the course of this study BEATTIE and coworkers [8] published an incomplete study of pentaphenylarsenic and pentaphenylantimony in solution. They suggested that these molecules retained their respective crystal geometries in solution, however there are many ambiguities remaining.

We have undertaken a complete vibrational study of these two molecules both in the solid state and in solution using Raman and infrared spectroscopy. Structural conclusions are based on the number and symmetry of the carbon metal-vibrations (termed  $\alpha$ -sensitive by WHIFFEN) [12].

### RESULTS and DISCUSSION

If one examines the vibrational modes of a monosubstituted benzene ring it is found that under the  $C_{2v}$  symmetry there will be 30 nondegenerate modes,  $11 A_1 + 3 A_2 + 10 B_1 + 6 B_2$ . Of these 30 vibrations, only six are sensitive to the mass of the substituent, these are Whiffen's  $\alpha$ -sensitive vibrations. In a molecule which contains more than one phenyl group there is a breakdown of the  $C_{2v}$  symmetry assumption for the monosubstituted benzene ring. The individual phenyl modes can couple to produce in-phase and out-of-phase vibrational modes. The number and symmetry of these modes will depend on the symmetry at the central atom. An analysis of this type has been developed for the stretching vibrations for a large number of point groups by MACKAY, SOWERBY and YOUNG [11]. Table 1 gives the number of expected phenyl-metal vibrations for trigonal bipyramidal and square pyramidal skeletal geometries. This analysis has been presented for both the bending and stretching vibrations. A graphical illustration of the normal modes for a square pyramidal molecule has been given by LEONE, SWANSON and SHRIVER [13].

Tables 2 and 3 give the observed vibrational frequencies below  $700 \text{ cm}^{-1}$  for pentaphenylarsenic and pentaphenylantimony respectively. The Raman spectra of pentaphenylantimony in the solid state and in methylene chloride solution are shown in Figs. 1 and 2 respectively.

Table 1. Allowed infrared and Raman vibrations for  $\text{Ph}_5\text{M}$  type molecules

Vibration*	Point group	IR active	Raman active
$g, r, t$ stretching	$D_{3h}$	$A_2'' + E'$	$2A_1 + E'$
$u, y, x$ bending	$D_{3h}$	$A_2'' + 2E'$	$2E' + E''$
$g, r, t$ stretching	$C_{4v}$	$2A_1 + E$	$2A_1 + B_1 + E$
$u, y, x$ bending	$C_{4v}$	$A_1 + 2E$	$A_1 + B_1 + B_2 + 2E$

\* Whiffen's notation, reference 12.

[11] K. M. MACKAY, D. B. SOWERBY and W. C. YOUNG, *Spectrochim. Acta. A*, **24**, 611 (1968).

[12] D. H. WHIFFEN, *J. Chem. Soc.* 1350 (1956).

[13] S. R. LEONE, B. SWANSON and D. F. SHRIVER, *Inorg. Chem.* **9**, 2189 (1970).

Table 2. Infrared and Raman spectra of pentaphenylarsenic (solid and solution) below 700  $\text{cm}^{-1}$ 

Raman		Infrared		Assignment*
Solid	Solution*	Solid	Solution*	
		691 vs	691 vs	$\nu(\nu_8, B_2)$ $\Phi(\text{C}-\text{C})$
667 m	668 m, dp			$r(\nu_2, A_1)$ $x$ -sensitive
659 m	658 s, p	655 w	660 w	
644 s	644 s, p	650 w	646 w	
		635 m	635 m	
618 m	617 m, dp	618 w	617 w	$s(\nu_{18}, B_1)$ $\alpha-(\text{C}-\text{C}-\text{C})$
		497 s	500 s	$Y(\nu_{19}', B_2)$ $x$ -sensitive
		473 m	478 m	
		469 s	472 s	
		462 s	464 s	
355 w	355 w	353 vs	352 vs	$t(\nu_{18}', A_1)$ $x$ -sensitive
297 w	299 w	296 vs	294 vs	
268 m				$u(\nu_{14}', B_1)$ $x$ -sensitive
260 m	260 m, dp	260 m	260 m	
244 m	244 m, dp	242 m	241 m	
220 vs	221 vs, p	226 m	228 m	
214 m	213 m, p	241 m	208 m	
201 m	206 w	200 m	203 m	$x(\nu_{20}', B_2)$ $x$ -sensitive
185 w	184 w			
175 m	175 m, dp	174 w	174 w	
165 w	166 w, dp			

\* Either dichloromethane or dibromomethane solution.

† The principal notation is that of WHIFFEN [12]. The notation in parenthesis has been adapted by Durig and coworkers<sup>78</sup> from Herzberg's numbering for the benzene modes in  $D_{6h}$  symmetry: G. HERZBERG, *Infrared and Raman Spectra of Polyatomic Molecules*, Vol. II, Van Nostrand, Princeton, N.J. (1945).

Of the six  $x$ -sensitive modes, five fall in the frequency region below 700  $\text{cm}^{-1}$ . The stretching mode  $q$  occurs at much higher frequency and is not very sensitive to changes in the local geometry. There are three bands which fall below 700  $\text{cm}^{-1}$  which are not  $x$ -sensitive and are invariant for both molecules. These ring modes are easily assigned and will not be discussed further.

The easiest modes to assign are the  $r$  and  $y$  modes. The  $r$  mode is a stretching vibration and is quite sensitive to changes in the local geometry. This band is very weak in the infrared but shows up clearly in the Raman spectra. In the Raman spectra of pentaphenylarsenic it is present as two intense polarized bands at 644 and 659  $\text{cm}^{-1}$ . There is also a weaker depolarized band at 668  $\text{cm}^{-1}$ . For pentaphenylantimony the  $r$  mode has four components two of which are polarized. The number of bands observed and the polarization is consistent with the known local geometry of these molecules. The  $y$  mode is absent from the Raman spectra but appears strongly in the infrared. This is present as four bands for pentaphenylarsenic while three strong absorptions are observed for pentaphenylantimony. For pentaphenylarsenic our observations are in good agreement with those of MACKAY, SOWERBY and YOUNG [11] but they do not report the very intense absorption at 475  $\text{cm}^{-1}$  for pentaphenylantimony.

Table 3. Infrared and Raman spectra of pentaphenylantimony (solid and solution) below  $700\text{ cm}^{-1}$ 

Solid	Raman		Infrared		Assignment†
	Solid	Solution*	Solid	Solution*	
			690 s	691 s	$\nu(\nu_8, B_2) \Phi(\text{C}-\text{C})$
			680 s		
			673 s		
662 m	663 w, dp		662 w		$r(\nu_2, A_1)$ $x$ -sensitive
659 m	659 w, dp				
654 s	655 s, p		655 w	655 w	
646 s	647 s, p		647 w		$s(\nu_{18}, B_1) \alpha-(\text{C}-\text{C}-\text{C})$
			475 s	469 s	$Y(\nu_{19}', B_2)$ $s$ -sensitive
			458 s	459 s	
			447 s	447 s	
	407 w, dp				$w(\nu_{20}, A_2) \Phi(\text{C}-\text{C})$
288 m	283 m	275 vs	280 vs		$t(\nu_{18}, A_1)$ $x$ -sensitive
266 m	266 m	267 vs	260 vs		
		242 w	240 w		
225 m	224 m, dp	227 w	220 z, br		$u(\nu_{14}', B_1)$ $x$ -sensitive
218 m	220 m, dp	215 w			
209 vs	210 vs	208 w	206 w		
202 m	202 m, p				
186 m	187 w, dp				$x(\nu_{20}', B_2)$ $x$ -sensitive
172 m					
162 w	162 w, dp	167 w	167 w		
	158 w, dp				

\* Either dichloromethane or dibromomethane solution.

† The principal notation is that of WHIFFEN [12].

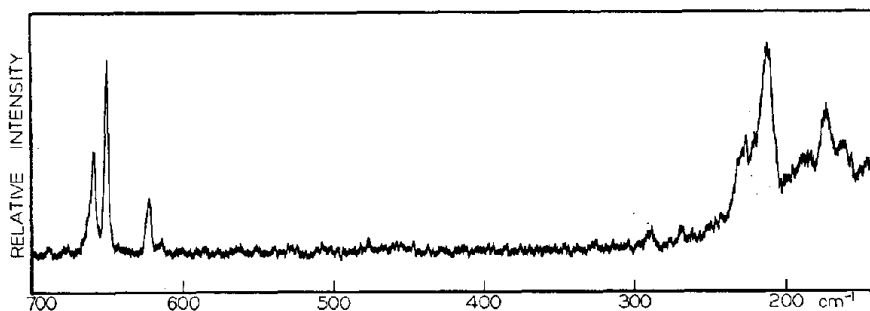


Fig. 1. The laser-Raman spectrum of pentaphenylantimony in the solid state.

The assignment of the  $t$ ,  $u$ , and  $x$  modes is a bit more difficult. These modes have a large number of bands occurring within a fairly narrow frequency range and in the solid state crystal field splittings may also occur for some of the bands [14].

Of all the  $x$ -sensitive modes, the  $t$  mode is the most sensitive to the mass of the substituent on the ring. The two strong absorptions at  $353$  and  $296\text{ cm}^{-1}$  in the infrared spectrum of pentaphenylarsenic are definitely part of the  $t$  mode. In the

[14] J. B. ORENBERG, M. D. MORRIS, and T. V. LONG, *Inorg. Chem.* **10**, 933 (1971).

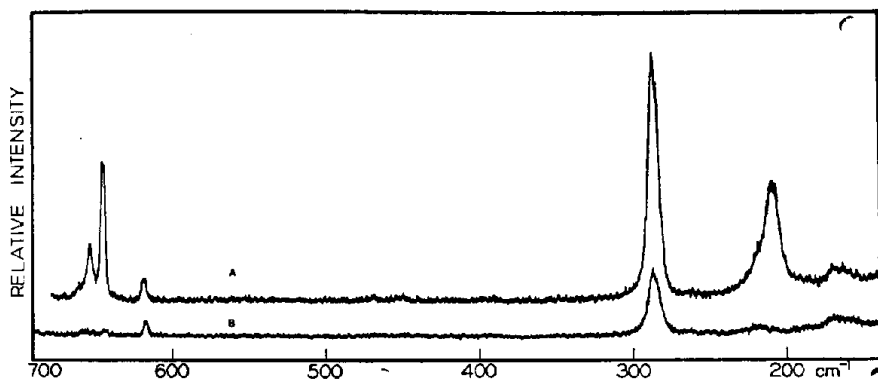


Fig. 2. The laser-Raman spectrum of pentaphenylantimony in methylenechloride solution. The strong band at  $278\text{ cm}^{-1}$  is due to the solvent. (A)  $I_{\parallel}$  (B)  $I_{\perp}$ .

infrared spectrum of tetraphenylarsenic (*V*) the *t* mode was observed as three bands  $375$ ,  $364$ ,  $345\text{ cm}^{-1}$  [14]. The large separation between the two components in pentaphenylarsenic is probably due to the difference between the equatorial and axial phenyl rings. The band at  $355\text{ cm}^{-1}$  is most likely the equatorial stretch while the lower frequency  $297\text{ cm}^{-1}$  band is due to the axial stretching motion of the rings. The *t* mode in pentaphenylantimony can be assigned to the 3 bands at  $275$ ,  $267$  and  $242\text{ cm}^{-1}$ . These bands are very broad and there may be additional components obscured by the intense adsorption of the two most intense components of this mode in the solution phase. In the solid the adsorptions are at  $275$  and  $267\text{ cm}^{-1}$  while in the solution phase these bands occur at  $280$  and at  $260\text{ cm}^{-1}$ . This is probably due to free rotation of the phenyl rings in the solution state.

The remaining bands are assigned to the *u* and *x* modes. For both pentaphenylarsenic and pentaphenylantimony there are a large number of band which fall below  $250\text{ cm}^{-1}$ . There is a very intense polarized band occurring at  $220\text{ cm}^{-1}$  for pentaphenylarsenic and at  $210\text{ cm}^{-1}$  for pentaphenylantimony. This band has been observed in the Raman studies of a large number of phenyl-metal compounds and is generally assigned to the *u* mode [15]. Four more bands are observed in the Raman spectra of pentaphenylarsenic which are probably components of the *u* mode. The band at  $268$  could be due to a crystalline splitting because it is not observed in the infrared or the solution spectra of the Raman. With pentaphenylantimony there are three additional bands which can be assigned to components of the *u* mode. The very low energy bands which remain can be assigned to the bending mode *x*. The exact number of bands is a bit difficult to determine because of their close proximity to each other and because they are quite weak in both the Raman in infrared spectra.

In comparison of the spectral data for pentaphenylarsenic and pentaphenylantimony it is quite evident that these molecules possess different skeletal geometries. This is evident both from the number of bands present from the different modes and the separation of the bands for the different modes. For pentaphenylarsenic which has  $D_{3h}$  skeletal symmetry there is generally a large separation

[15] J. R. DURIG, C. W. SINK and J. B. TURNER, *Spectrochim. Acta* **26A**, 557 (1970).

between the lowest frequency component and the highest frequency component of a given mode. This is due to the differences between the axial and equatorial phenyl rings. With pentaphenylantimony the crystal structure shows four phenyl rings slightly below the basal plane and one in the axial position. There is less coupling between the rings in this geometry and less separation is observed between the bands. The solution spectra for pentaphenylarsenic are almost identical to that for the solid state. A couple of bands are not observed in the solution spectra which were observed in the solid state spectra but this is due to removal of the crystalline field interactions and not to a change in geometry. This effect is also observed in the spectra of pentaphenylantimony. While the NMR spectra show that both of these molecules are stereochemically nonrigid systems on the NMR time scale there is no evidence for this behavior in the vibrational spectra. It is clear that both of these molecules retain their respective solid state geometries in solution.

#### EXPERIMENTAL

Pentaphenylarsenic was prepared by the addition of phenyllithium to tetraphenylarsenic bromide [16]. The crude product was recrystallized from isooctane and gave large white crystals. Pentaphenylantimony was prepared by the addition of phenyllithium to triphenylantimony dichloride [17]. Following hydrolysis of the lithium hexaphenylantimonate. The crude pentaphenylantimony was recrystallized from isooctane. The pentaphenylantimony formed in this had a slight yellow color but this could be removed by dissolving the recrystallized product in a minimum amount of benzene and precipitating the pentaphenylantimony with methanol.

Raman spectra were recorded on a modular instrument employing a Spex Model 1400-II double monochromator, and a ITT FW-130 photomultiplier tube with an S-20 response curve. Either d.c. amplification or photon rate-metering was used. The 6328 Å line of a Spectra-physics Model 125 helium-neon laser was used for excitation of the solid samples. The solid samples were lightly packed into melting point capillary tubes and run at room temperature. The solution spectra were recorded using a Coherent Radiation Model 54 argon-ion laser for excitation. At room temperature decomposition of the solution samples led to fluorescence, thus these samples were cooled to approximately  $-30^{\circ}$ . No change was noted in the Raman spectra with a decrease in temperature. Solutions were made up in either dichloromethane or dibromomethane with the concentration of pentaphenylarsenic or pentaphenylantimony about one molar. All solutions were filtered through a Millipore filter prior to measurement of the Raman spectra. Polarization measurements were made with a polaroid film analyzer placed in front of the entrance slit to the monochromator. The spectrometer was calibrated using the emission lines from the laser.

Infrared spectra below  $400\text{ cm}^{-1}$  were recorded on a Digilab Model FTS 16/20 Fourier transform infrared spectrometer. The resolution was computer controlled to  $0.5\text{ cm}^{-1}$ . Infrared measurements above  $400\text{ cm}^{-1}$  were made using a Beckman IR-12 grating infrared spectrometer. Both infrared spectrometers were purged with dry nitrogen. Solid samples were run as Nujol mulls using either polyethylene

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[16] G. WITTIG and K. CLAUS, *Ann. Chem.*, **577**, 26 (1952).

or potassium chloride plates. The solution spectral below  $400\text{ cm}^{-1}$  were recorded in polyethylene cells with a path length of 0.2 mm. Sealed potassium bromide cells were used for the infrared measurements about  $400\text{ cm}^{-1}$ . Both infrared spectrometers were calibrated using water vapor. The observed frequencies are accurate to  $\pm 2\text{ cm}^{-1}$  for the stronger bands and to  $\pm 5\text{ cm}^{-1}$  for the weaker broader bands. A Dupont Model 310 curve resolver was used in the analysis of the Raman Spectra below  $300\text{ cm}^{-1}$ . This aided in frequency placement of the overlapping bands.

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