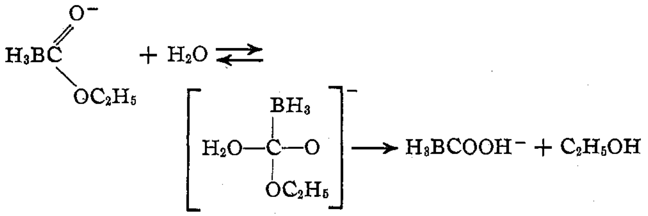
reaction in water is suggested. In this case, the mechanism may involve an intermediate with the solvent water and subsequent reactions as shown in



$$H_3BCOOH^- + OH^- \longrightarrow H_3BCO_2^{2-} + H_2O$$

In any case these results indicate that the *O*-ethylboranocarbonate ion and the normal monoethylcarbonate ion hydrolyze by the same rate law with comparable rate constants (*i.e.*, for $OCO_2C_2H_5$ at 0°, $k = 0.00102$ min^{-1}).[6]

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Four- and Five-Coordination in Tetraphenyl Derivatives of Phosphorus(V), Arsenic(V), and Antimony(V). An Investigation Employing Laser-Raman Spectroscopy[1]

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The laser-Raman spectra of a number of crystalline tetraphenylphosphorus(V), tetraphenylarsenic(V), and tetraphenylantimony(V) compounds are measured in order to differentiate tetracoordinate species from those that are pentacoordinate. Structural conclusions are based on the spectra in the low-frequency ("X-sensitive") region, and the crystalline P(V) and As(V) compounds appear to be four-coordinate. This is also true for $(C_6H_5)_4SbClO_4$, but there is evidence that the other Sb(V) derivatives are pentacoordinate and probably trigonal bipyramidal in the solid state. All compounds studied are tetracoordinate in methanolic solution, with the exception of the molecular species $(C_6H_5)_4SbF$. The existence of the five-coordinate cations $(C_6H_5)_4SbOH_2^+$ and $(C_6H_5)_4AsOH_2^+$ in aqueous solutions of the corresponding salts is possible.

An examination of earlier literature reveals X-ray diffraction studies that demonstrate the existence of discrete tetrahedra for the $(C_6H_5)_4P^+$ and $(C_6H_5)_4As^+$ cations in the solid state.[3–5] Several recent observations[6,7] suggest that five-coordination is a general phenomenon in tetraphenylantimony derivatives, contrasting with the ionic structures of the stoichiometrically similar arsenic and phosphorus salts. Within the last year, structural studies of methoxytetraphenylantimony[8] and hydroxytetraphenylantimony[9] have shown that both molecules are pentacoordinate trigonal bipyramids with OCH_3 and OH groups, respectively, in one of the axial positions. An additional question that warrants investigation is whether a square-pyramidal or trigonal-bipyramidal coordination polyhedron is adopted, since the sole pentacoordinate compound among those formed by P(V), As(V), and Sb(V) that has been shown to deviate from trigonal-bipyramidal geometry is pentaphenylantimony.[10,11]

The cations are useful as potentiometric and amperometric titrants,[12–15] and it is interesting to note that while both $(C_6H_5)_4P^+$ and $(C_6H_5)_4As^+$ exhibit single, two-electron polarographic waves,[16,17] the reduction of $(C_6H_5)_4Sb^+$ proceeds through two discrete one-electron transfers.[18] The key to this anomalous polarographic behavior may be in the geometries adopted by these species in solution.

In this investigation we employ vibrational measurements in the region below 700 cm^{-1} to differentiate between four- and five-coordination in tetraphenyl derivatives of P(V), As(V), and Sb(V) in the crystalline state and in aqueous and methanolic solutions. Structural conclusions are based on the number and symmetries of fundamentals involving phenyl–central atom motions (termed "X sensitive" by Whiffen[19]), which are deter-

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mined by the total molecular geometry[20,21] rather than by the idealized C_{2v} symmetry of a monosubstituted benzene ring.

Experimental Section

Materials.—Tetraphenylantimony bromide (City Chemical Corp.) was recrystallized through the addition of cold ether to a charcoal-filtered ethanolic solution of the compound (mp 207–212°). Tetraphenylantimony sulfate was prepared as previously described[18] and converted through ion exchange [Rexyn Ag 1 ($Cl^- - SO_4^{2-}$) resin] to tetraphenylantimony chloride with recrystallization as above (mp 209–210°). Tetraphenylantimony fluoride and tetraphenylantimony perchlorate were prepared by the addition of sodium fluoride and dilute $HClO_4$ solutions, respectively, to a solution of tetraphenylantimony sulfate. The hydroxytetraphenylantimony was prepared by the addition of excess ammonium hydroxide to a solution of tetraphenylantimony bromide. Tetraphenylarsenic chloride (City Chemical Corp.) was recrystallized (mp 277–281°), and tetraphenylarsenic carbonate was produced by addition of Ag_2CO_3 to the chloride salt. The carbonate was neutralized with excess sulfuric acid to give a solution of tetraphenylarsenic sulfate, and tetraphenylphosphorus sulfate was prepared similarly from tetraphenylphosphorus chloride (K & K Laboratories, Inc.; mp 273–275°).

The methanolic solutions were prepared with spectrophotometric grade methanol and were of the following approximate concentrations: 0.5 *M* $(C_6H_5)_4PCl$, 0.3 *M* $(C_6H_5)_4AsCl$, 0.1 *M* $(C_6H_5)_4SbCl$, and 0.3 *M* $(C_6H_5)_4SbF$. Saturated aqueous solutions of the three chloride salts were prepared, and aqueous solutions of the sulfates were of the following approximate concentrations: 0.5 *M* $[(C_6H_5)_4P]_2SO_4$, 0.15 *M* $[(C_6H_5)_4As]_2SO_4$, and 0.15 *M* $[(C_6H_5)_4Sb]_2SO_4$. The aqueous chloride solutions exhibited a pH range of 5.4–6.6, while the aqueous sulfate solutions were of pH 1.8–1.9. All solutions were filtered one or more times through sintered-glass or Millipore filters (Solvinert or Millipore type) prior to measurement of their Raman spectra.

Instrumentation.—All laser-Raman Spectra were recorded with a modular instrument employing a Spex Model 1400-II double monochromator spectrometer, an ITT FW-130 phototube with S-20 response, and a dc amplifier. The excitation source was a Spectra-Physics Model 112 helium–neon laser utilizing the 6328-Å line as the exciting frequency (monitored power *ca.* 30 mW). This was calibrated in the region 0–4000 cm^{-1} using known frequencies of certain neat liquids and neon lines. For solution spectra the error in observed frequencies is ± 3 cm^{-1}, except for broad bands where the frequencies are accurate to ± 5 cm^{-1}, and a smaller error is anticipated for the stronger peaks in the spectra of the solids. Spectra of solids were obtained by reflection from lightly pressured microcrystalline pellets that were mounted on a goniometer head at an angle of 20° to the incident laser beam. The spectra of all solids and solutions were measured under a number of resolution conditions, ranging from 5 to 10 cm^{-1} for the solutions and from 2.5 to 5 cm^{-1} for the solid materials. The spectra in the region beyond 2500 cm^{-1} were adequately observed only with 10-cm^{-1} resolution slits, while the region below 120 cm^{-1} was measured using 1.0–2.5-cm^{-1} spectral resolutions. Analysis employing a Du Pont Model 310 curve resolver was used to aid in frequency placement for the bands found between 100 and 350 cm^{-1} in the spectra of the aqueous solutions. Depolarization ratios were measured by rotating a Polaroid film analyzer in the scattered beam, and the polarization of the scattered light was subsequently scrambled before entering the spectrometer. Infrared spectra of the compounds in potassium bromide pellets and in Nujol mulls supported on cesium iodide plates were measured with a Perkin-Elmer Model 621 grating infrared spectrometer purged with dry air. This instrument was calibrated using water vapor and polystyrene film, and the observed infrared frequencies are accurate to better than ± 2 cm^{-1}. All Raman and infrared intensities are reported relative to other bands in the same spectrum.

Results and Vibrational Assignments

Frequency Region above 700 Cm^{-1}.—The vibrational spectra of phenyl-containing moieties may be analyzed either in terms of the total molecular symmetry (phenyl group orientation is neglected) or through the approximate device of ascribing observed frequencies to modes of a single, monosubstituted benzene ring of C_{2v} symmetry. The latter approximation yields 30 nondegenerate modes of symmetry $11\ A_1 + 3\ A_2 + 10\ B_1 + 6\ B_2$, and such a description is appropriate to the frequency region above 700 cm^{-1}. Of the 30 fundamentals, all but 6 are characterizable as insensitive to the molecular symmetry and to the nature or mass of the substituent group. The 6 symmetry- and substituent-sensitive vibrations are termed X sensitive.[19] Only a single X-sensitive vibration appears above 700 cm^{-1}, the A_1 fundamental q, which occurs at (1110, 1097), 1086, and 1067 cm^{-1} in $(C_6H_5)_4PCl$, $(C_6H_5)_4AsCl$, and $(C_6H_5)_4SbCl$, respectively.

The infrared and Raman spectra are not reported in detail for the region above 700 cm^{-1}, although they are available from the authors. Within the above symmetry considerations this seems unnecessary, since they are in excellent agreement with the painstaking studies of Durig and coworkers on phenyl derivatives of Si, Ge, and Sn[21–23] and Smith's investigations, also of group IVa compounds.[24,25] Infrared measurements on phenylphosphorus, -arsenic, and -antimony molecules[26–32] are plentiful, and, in particular, our data are in good correspondence to the absorption spectra (above 250 cm^{-1}) that are available for tetraphenylphosphorus,[33] tetraphenylarsenic,[20] and tetraphenylantimony compounds. However, no Raman data are evident for phenyl-containing P(V), As(V), or Sb(V) compounds, although partial Raman spectra of triphenylphosphine,[30,34] triphenylarsine,[31,34] and triphenylstibine[34] have been recorded.

The Raman spectra of tetraphenyl compounds with chloride or sulfate as a counterion are identical in this region, except for additional bands attributable to sulfate internal motions, and there is no evidence of factor group or site group perturbations. Depolarization ratios were measured for lines of sufficient intensity in the spectrum of the $(C_6H_5)_4PCl$ aqueous solution, and they are invariably congruent with the proposed assignments.[21–23] Notably, the A_1 symmetry mode k at 1589 cm^{-1}, which curiously appears to be depolarized in the spectra of phenylgermanes,[22,23,35] is found to be moderately polarized, and this is consistent with its observation as a polarized shift at 1548 cm^{-1} in C_6D_5Br.[36]

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TABLE I

LASER-RAMAN AND INFRARED SPECTRA OF $(C_6H_5)_4PCl$ (SOLID AND AQUEOUS) AND $(C_6H_5)_4AsCl$ (SOLID) IN THE X-SENSITIVE REGION[a]

$(C_6H_5)_4PCl$			$(C_6H_5)_4AsCl$		
Infrared (solid)	Raman (solid)	Raman (aqueous soln)	Infrared (solid)	Raman (solid)	Assignment
687 s[b]	682 ms	681 ms, dp	692 vs	695 w	v (ν_8, B_2)—Φ (C–C)[d]
			688 vs	680 m	
687 s	682 ms	681 ms, p	670 w	670 s	r (ν_2, A_1)—X sensitive
611 w	616 ms	616 ms, dp	613 w	614 ms	s (ν_{18}, B_1)—α (C–C–C)
526 vs	529 vw	535 vw		505 vw	y (ν'_{19}, B_2)—X sensitive
486 vw	480 vw	506 vw	475 s	480 vw	
			463 vs	464 vw	
			452 w	448 vw	
454 vw	463 w	455 vw, br	375 w	370 vw	t (ν'_{18}, A_1)—X sensitive
431 w	435 w		364 s	350 w	
			345 vs		
	400 vw, br	400 vw, br[c]	405 vw	400 vw	w (ν_{20}, A_2)—Φ (C–C)
			398 vw		
283 w	285 mw	285 m, dp		267 vw, sh	u (ν'_{14}, B_1)—X sensitive
	281 mw			261 ms	
270 w	257 s	250 s, p	245 s	245 w, sh	
	250 w, sh			239 s	
	209 m	197 ms, dp		186 m	x (ν'_{20}, B_2)—X sensitive
	202 m				
	195 mw				

[a] The spectra of the corresponding sulfate salts and $(C_6H_5)_4AsF$ are identical with those of the chloride salts except for additional bands attributable to SO_4^{2-} fundamentals. [b] Abbreviations used in Tables I–III: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; p, polarized; dp, depolarized. [c] H_2O libration, also. [d] The principal modal designation is that suggested by Whiffen,[19] while the notation adopted by Durig and coworkers[21–23] is given in parentheses. The latter notation employs the numbering used by Herzberg for benzene modes in D_{6h} symmetry, and the primed and unprimed terms distinguish between vibrations arising from motions whose degeneracy is removed upon ring substitution: G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, p 118.

TABLE II

LASER-RAMAN SPECTRA OF TETRAPHENYLANTIMONY(V) SOLIDS IN THE X-SENSITIVE REGION

$[(C_6H_5)_4Sb]ClO_4$	$(C_6H_5)_4SbF$	$(C_6H_5)_4SbCl$	$(C_6H_5)_4SbBr$	$(C_6H_5)_4SbOH$	$[(C_6H_5)_4Sb]_2SO_4$	Assignment
694 vw	696 vw	693 vw, br	699 vw	703 vw	695 vw	v (ν_8, B_2)—Φ (C–C)
	664 m					
665 s	658 m	661 m	666 m	660 s	660 m	r (ν_2, A_1)—X sensitive
	652 vs	654 vs	658 vs	652 ms	650 vs	
627 w						ν_4 (ClO_4^-)
617 w	621 m	617 m	619 m	622 m	617 m	s (ν_{18}, B_1)—α (C–C–C)
					589 mw	ν_4 (SO_4^{2-})
					575 w	
				533 mw		ν (Sb–O)
			510 vw	510 vw		
					462 w	ν_2 (SO_4^{2-})
					437 mw	
460 mw	455 vw, br	455 w, br	462 w, br	461 vw	453 w	y (ν'_{19}, B_2)—X sensitive and ν_2 (ClO_4^-) in $(C_6H_5)_4SbClO_4$
446 mw				448 w		
	406 mw	392 vw	399 vw	397 vw	405 w	w (ν_{20}, A_2)—Φ (C–C) and ν (Sb–F) in $(C_6H_5)_4SbF$
		353 vw				ν (Sb–Cl)
315 w	294 m	291 m	296 mw	305 w	298 mw	t (ν'_{18}, A_1)—X sensitive
291 m	279 m			291 m	279 m	
				270 w, br		
			263 vs			ν (Sb–Br)
252 m	257 m	258 s	263 vs	244 sh	248 sh	u (ν'_{14}, B_1)—X sensitive
239 vs	236 ms	233 s	238 s	234 m	238 vs	
220 w, sh	218 vs	223 vs	229 vs	216 vs	225 vs	
	212 vs	211 vs	211 vs	208 vs	215 vs	
	198 m	191 s	195 m	193 m		x (ν'_{20}, B_2)—X sensitive
	150 ms	156 s	154 mw	162 m	165 sh	
140 w		130 w, sh			132 s	Lattice mode (?)

X-Sensitive Frequency Region.—Table I contains the low-frequency Raman spectra of $(C_6H_5)_4PCl$ in solid and solution phases and the vibrational spectra of solid $(C_6H_5)_4AsCl$, while Table II contains the relatively richer Raman spectra of a number of tetraphenylantimony salts. Table III compares the spectra of $(C_6H_5)_4SbCl$ in all phases with that of an aqueous solution of $(C_6H_5)_4AsCl$.

Figures 1 and 2 contrast the spectra of solid $(C_6H_5)_4SbClO_4$ and $(C_6H_5)_4SbCl$, respectively, and Figures 3 and 4 contain the low-frequency spectra of aqueous solutions of $[(C_6H_5)_4As]_2SO_4$ and $(C_6H_5)_4SbCl$. In lower portions of Figures 3 and 4 the spectra with the sloping Rayleigh backgrounds removed utilizing a Du Pont Model 310 curve resolver are shown. Curve resolution is also employed to arrive at the best estimate of peak frequency placement, although the existence of the reported bands is evident from the total band contours without resolution.

The frequency region below 700 cm^{-1} contains five of the six X-sensitive fundamentals and three bands that are unaffected by the nature of the phenyl sub

Table III

Laser-Raman Spectra of $(C_6H_5)_4SbCl$ and $(C_6H_5)_4AsCl$ Solutions in the X-Sensitive Region

$(C_6H_5)_4SbCl$			$(C_6H_5)_4AsCl$	
Raman (solid)	Raman (aqueous)	Raman (methanol)	Raman (aqueous)	Assignment
693 vw, br	697 w, br		689 w	v (ν_8, B_2)—Φ (C–C)
661 m	663 ms	658 ms	674 ms	r (ν_2, A_1)—X sensitive
654 s				
617 m	618 m	615 w	615 mw	s (ν_{18}, B_1)—α (C–C–C)
	508 vw, br			ν (Sb–OH_2) (?)
455 w, br	452 vw, br		511 w	y (ν'_{19}, B_2)—X sensitive
392 vw				w (ν_{20}, A_2)—Φ (C–C)
353 vw				ν (Sb–Cl)
291 m	286 m, p (?)	276 w		t (ν'_{18}, A_1)—X sensitive
258 s	260 ms, dp		264 mw	u (ν'_{14},B_1) —X sensitive
233 s			285 w, dp	
223 vs	220 vvs, p	220 vs	242 vs, p	
211 vs				
191 s	192 ms, dp		209 mw, dp	x (ν'_{20}, B_2)—X sensitive
165 s	167 s, dp	167 w	184 s, dp	
156 s			152 mw, dp	
130 w, sh				Lattice mode (?)

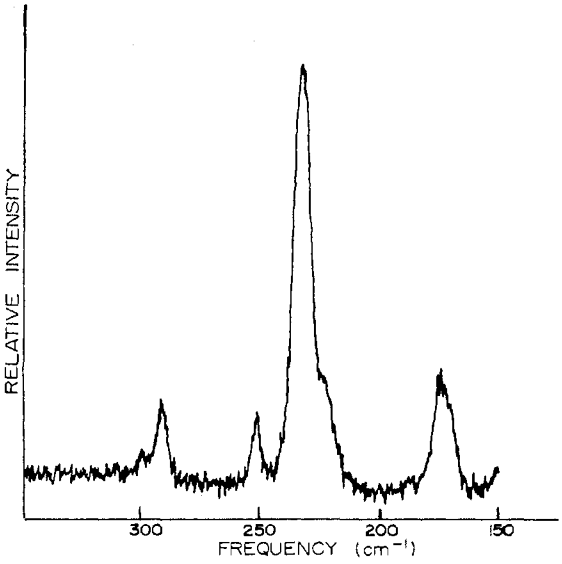

Figure 1.—The laser-Raman spectrum (350–150 cm^{-1}) of crystalline $(C_6H_5)_4SbClO_4$.

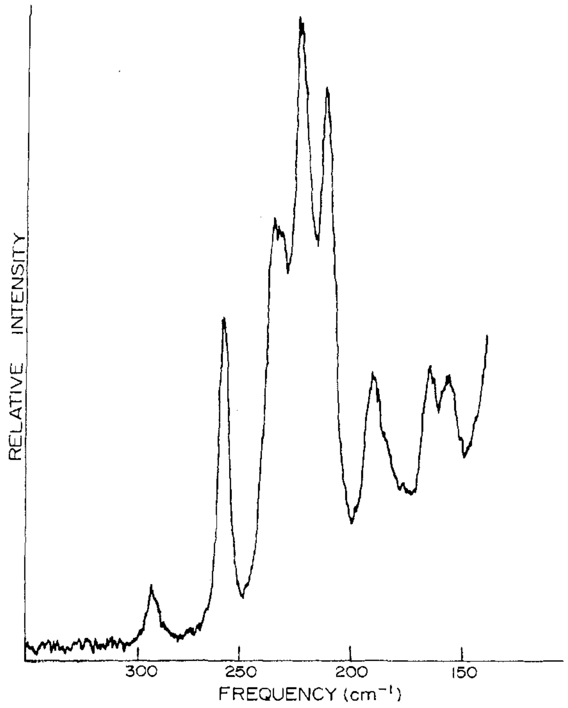

Figure 2.—The laser-Raman spectrum (350–150 cm^{-1}) of crystalline $(C_6H_5)_4SbCl$.

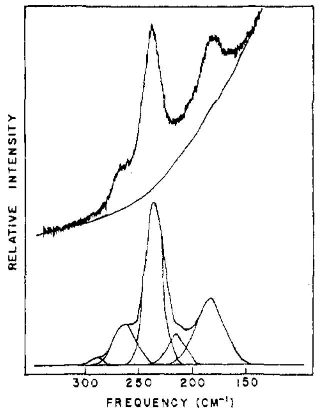

Figure 3.—The laser-Raman spectrum (350–125 cm^{-1}) of an aqueous solution of $[(C_6H_5)_4As]_2[SO_4]$ and curve resolution of the spectrum.

stituent. For the latter bands (v and w, out-of-plane ring deformations, and s, an in-plane ring deformation) assignments concordant with those suggested by Mackay, Sowerby, and Young[20] for the tetraphenyl compounds are made. These modes will not be discussed further, since they are frequency invariant for all group V compounds considered below.

Assignment of the X-sensitive bands requires a more cautious analysis, for in addition to a modal frequency dependence on the nature and mass of the substituent on the benzene ring, the spectra are complicated by a breakdown in the C_{2v} symmetry assumption. Each of the nondegenerate fundamentals of a phenyl group can combine with the corresponding vibrations of the other three phenyls attached to the same central atom under the appropriate molecular symmetry (or local symmetry about the central atom) to produce additional modes. This complication has been acknowledged in several previous papers,[20,21,25,37] and it would seem possible to turn this constructively so as to discern modifications in the local symmetry about the central atom in a series of related compounds or for a given molecule in crystalline and solution environments. For tetrahedrally disposed phenyl groups in the tetraphenyl derivatives, each of the X-sensitive A_1 modes in C_{2v} symmetry (labeled by Whiffen[19] q, r, and t) may combine with the corresponding vibration of the other three phenyl rings to produce two modes, one in which all phenyls move in phase (A_1 in T_d local symmetry) and a triply degenerate out-of-phase motion (F_2 under T_d symmetry). Moreover, the u modes (B_1 symmetry in C_{2v}) may also combine to produce one in-phase and one out-of-phase mode. Thus, four A_1 symmetry and four F_2 symmetry X-sensitive bands would be anticipated, and three of each will lie below 700 cm^{-1} under T_d local symmetry. For trigonal-bipyramidal local stereochemistry, with the four phenyls occupying one apical and three equatorial positions and a fifth group at the remaining apex (C_{3v} local symmetry) three Raman- and infrared-active vibrations (2 A_1 + E) may arise from

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[37] J. R. Durig, C. W. Sink, and J. B. Turner, *Spectrochim. Acta,, Part A*, **26**, 557 (1970). We thank Professor Durig for making a copy of this article available to us prior to publication.

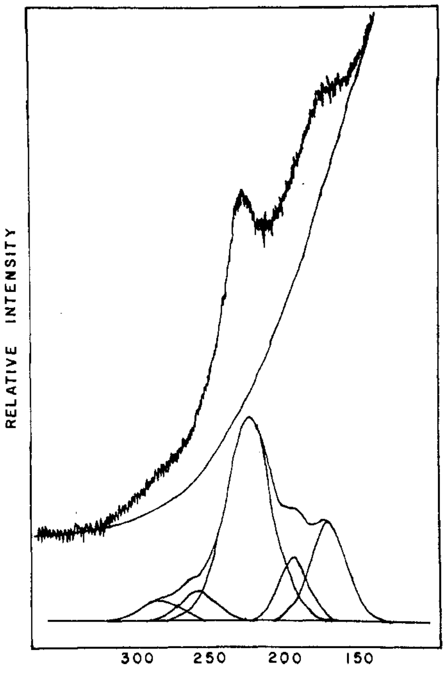

Figure 4.—The laser-Raman spectrum (350–125 cm^{-1}) of $(C_6H_5)_4SbCl$ in aqueous solution and curve resolution of the spectrum.

each of the phenyl modes q, r, t, and u. For pentacoordination with the fifth group in an equatorial rather than apical position (C_{2v} local symmetry), each of these phenyl-substituent modes may combine to form four nondegenerate vibrations. For solid materials, additional crystalline field splittings of the X-sensitive bands may occur and the phenyl group orientation may also yield a lower molecular symmetry than the local symmetry assumed above.

The fundamentals of primary structural significance are the r, t, u, and x modes.[19] For the tetraphenyl compounds of P(V), As(V), and Sb(V) the bands arising from the out-of-plane bending motion y are interesting only in that they appear at values nearly identical with those in the corresponding triphenylphosphine, -arsine, and -stibine[34] and are apparently insensitive to the change in oxidation number. Vibration t is an A_1 (under C_{2v} symmetry) stretching mode, involving motion of a phenyl ring against the central atom, and this mode is strongly X sensitive, appearing variously between 500 and 200 cm^{-1}. For the phosphorus compound this vibration is associated with two bands measured at 463 and 435 cm^{-1} in the Raman spectrum of the solid salt, consistent with the known T_d local symmetry.[3] This fundamental is located at 435 cm^{-1} in the infrared spectrum of tetraphenylsilane[25] and at (433, 403 cm^{-1}) in the spectrum of triphenylphosphine.[30,34] The t mode is placed at *ca.* 350 cm^{-1} for tetraphenylarsenic(V), since it appears at *ca.* 310 cm^{-1}[30,34] in the infrared spectrum of triphenylarsine and at 297 and 332 cm^{-1} in the spectra of triphenylgermane[21] and tetraphenylgermane,[25,37] respectively. Four infrared components of this vibration for $(C_6H_5)_4AsCl$ are recorded and crystalline splitting of the degenerate stretch could be important, but only two weak modes could be detected in the laser-Raman spectrum of the solid. Bands observed between 300 and 250 cm^{-1} in the spectra of the solid antimony compounds are assigned to the t mode, since this vibration is located at (272, 257 cm^{-1}) in $(C_6H_5)_4Sn$.[25]

Two alternatives present themselves for the assignment of the peaks at slightly lower energy (*e.g.*, between 200 and 250 cm^{-1} for the antimony compounds). For the homologous series $(C_6H_5)_4M$ (M = Si, Ge, Sn, Pb), Smith[25] has suggested that the weak infrared absorptions in this region are attributable to mode u, but he has assigned the relatively intense, polarized Raman band to a component of the t vibration. In support of this choice,[24] he argues that the components of the t vibration, corresponding to symmetric and asymmetric silicon–phenyl stretching motions, should be similar in frequency to analogous bromine–silicon stretches in the bromochlorosilanes. Other workers[20,23] have preferred an assignment of similar peaks in the spectra of phenyl–germanium derivatives to components of mode u. This position has been substantiated by Durig, *et al.*,[37] who based their arguments on the varying sensitivity of the t and u fundamentals of $(C_6H_5)_4Ge$ to deuteration, and we follow them in assigning the strong polarized bands in this region to the fully symmetric component of the u mode. The remaining group of low-frequency lines in each of the spectra is associated with mode x. Although these vibrations lie beyond the low-energy limit of most infrared absorption measurements, in the instances where they are recorded[21,31] this assignment is made.

Antimony–Anion Frequencies.—In the laser-Raman spectra of the solid tetraphenylantimony derivatives, additional lines appear that may be characterized as antimony–anion stretching modes. In crystalline $(C_6H_5)_4SbF$, a strong absorption occurs at 401 cm^{-1}, and this band is also observed in the infrared spectrum of a methanolic solution of $(C_6H_5)_4SbF$ at 404 cm^{-1}.[6] It is attributed to the Sb–F stretch because only the weak w vibration occurs near this frequency in other tetraphenylantimony derivatives. The Raman complement of this band appears at 406 cm^{-1}, and this peak is of greater intensity than generally observed for mode w. For solid $(C_6H_5)_4SbCl$, a weak Raman shift is measured at 353 cm^{-1} which may be due to the Sb–Cl band, since in the spectrum of $SbCl_5$ an antimony–chloride stretch appears at 356 cm^{-1}.[38] In the infrared spectra of $(C_6H_5)_2SnCl_2$ and $(C_6H_5)_3SnCl$, tin–chloride stretching frequencies are observed at 360 and 344 cm^{-1}, respectively,[25] and one may expect that the Sb–Cl frequency would not differ greatly from these values. However, the assignment of the Sb–Cl stretch as a contributor to the intensity of the 291-cm^{-1} band cannot be excluded. Mackay, *et al.*,[20] assigned the Sb–Cl modes of $(C_6H_5)_3SbCl_2$ to infrared peaks at 279 and 268 cm^{-1}, but they did not make an assignment for this mode in their infrared spectrum of $(C_6H_5)_4SbCl$. Although a discrete line characterizable as an Sb–Br vibration does not appear in the Raman spectrum of $(C_6H_5)_4SbBr$, the peak at 263 cm^{-1} is abnormally intense relative to other antimony compounds, and this may be due to an accidental degeneracy of this motion with a component of the t vibration. The infrared spectra of tetrahedral alkyltin bromides exhibit tin–bromine stretches in a frequency range around 250 cm^{-1},[39] and the Sb–Br band should lie in the region.

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For hydroxytetraphenylantimony(V), the antimony–hydroxide stretch was assigned to a band at 528 cm^{-1} in the infrared spectrum,[9] and this peak appears at 533 cm^{-1} in the laser-Raman spectrum and at 527 cm^{-1} in the infrared spectrum of the material examined herein. The Sb–OH bending mode[9] is also recorded at 793 cm^{-1}. No frequencies that would connote the presence of $(C_6H_5)_4Sb-O-Sb(C_6H_5)_4$[24] are measured for the freshly prepared hydroxide. The low-frequency Raman spectrum of $[(C_6H_5)_4Sb]_2SO_4$ exhibits bands at 575, 462, and 437 cm^{-1} that are probably solid-state-split ν_2 (*ca.* 600 cm^{-1}) and ν_4 (*ca.* 450 cm^{-1}) internal modes of the sulfate ion. These modes may also contribute to the intensity of the lines at 617 and 453 cm^{-1}. A band associated with an antimony–sulfate stretch was not found, but this vibration may enhance the strength of the shift observed at 238 cm^{-1}. In solutions of $In_2(SO_4)_3$, a line at 255 cm^{-1} is assigned to the analogous indium–oxygen stretch.[40] Goel,[41] on the basis of infrared data alone, has recently reached a number of these conclusions.

Discussion

The structures of tetraphenylantimony(V) compounds in solution and crystalline phases are of interest, since both four- and five-coordinate species have been observed.[6,42,43] In $(C_6H_5)_4SbClO_4$ it is unlikely that the perchlorate group is coordinated, and the low-frequency Raman spectrum of $(C_6H_5)_4SbClO_4$, shown in Figure 1, is identical in appearance with those of the crystalline tetraphenylphosphorus(V) and tetraphenylarsenic(V) salts. Briefly summarized, the pertinent features of the spectra of these tetrahedral species are as follows. A single component of mode r is measured in the region 700–650 cm^{-1}; two weak-to-medium intensity t modes occur, followed by a medium weak component of the u vibration; a strong u mode appears in the range 260–240 cm^{-1} (polarized in solution spectra) with only a slight shoulder to lower energy; and, finally, a single x fundamental is evident. In solid $(C_6H_5)_4PCl$, crystalline field splittings of the weak component of mode u and the x vibration are measured.

The spectra should be contrasted with the Raman spectra of $(C_6H_5)_4SbOH$, known to be five-coordinate and trigonal bipyramidal,[9] and of $(C_6H_5)_4SbF$, for which there is also good evidence of pentacoordination.[6,41] The spectra of these antimony species differ from the spectra of the tetracoordinate salts as follows. In the spectra of the pentacoordinate compounds the r mode appears with two strong components rather than one, and the high-frequency component of the u fundamental is relatively more intense; the strong component of mode u is broader, and it is strongly split by either phenyl group coupling or crystalline perturbations; and vibration x is measured as two moderately intense lines at *ca.* 195 and *ca.* 165 cm^{-1}, rather than a single band (two components of the lower frequency line appear, again presumably due to coupling or solid-state effects). The spectra of the remaining antimony derivatives in Table II, with the possible exception of the sulfate derivative, closely resemble those of the pentacoordinate molecules, and this suggests that five-coordination is common for tetraphenylantimony(V) compounds in the solid state. Additionally, each spectrum contains a band that may be assigned principally to an antimony–anion stretch (*vide supra*). The qualitative spectral differences that we believe differentiate four- and five-coordination for the group V tetraphenyl species are most clearly seen by comparing the spectra in Figures 1 and 2. The conclusion that the crystalline tetraphenylantimony(V) derivatives except for the perchlorate and, possibly, the sulfate are molecular rather than ionic compounds is thus based on the following aspects of the Raman spectra in the low-frequency region: (a) the increase in the number of components of the X-sensitive fundamentals over that found for the tetrahedral species, which is predicted for pentacoordination by the coupling arguments given above; (b) the spectra in the X-sensitive region are identical with those of the known five-coordinate species $(C_6H_5)_4SbOH$[9] and $(C_6H_5)_4SbF$;[6,41] and (c) new shifts appear in the proper region for antimony–anion stretching modes in each case. Point (b) also implies that the compounds are trigonal bipyramidal rather than square pyramidal.

The simplicity of the spectra of $(C_6H_5)_4PCl$ in aqueous solution (Table I) and of $(C_6H_5)_4SbCl$ in methanol (Table III) suggests that in both cases a four-coordinate cation is present. The spectra of the phosphorus compound in aqueous and crystalline phases are the same except for solid-state-induced splittings of modes t, u, and x; the spectrum of the methanolic antimony solution resembles that of solid $(C_6H_5)_4SbClO_4$ (Figure 1). In the methanol medium, dissolution is apparently accompanied by ionization of the chloride, and the solvent does not participate in first-coordination sphere binding to the antimony atom. The spectra of methanolic solutions of tetraphenylarsenic(V) chloride and sulfate salts (not reported) similarly indicate that tetrahedral cations are present. In contrast to this, for a methanolic solution of $(C_6H_5)_4SbF$, lines are measured at 296 and 272 cm^{-1} (t mode), 222 and 208 cm^{-1} (u mode), and 182 and 154 cm^{-1} (x mode). There is abundant evidence that $(C_6H_5)_4SbF$ behaves as a pentacoordinate nonelectrolyte in various organic solvents.[6,41] The components of the u and x modes found in the $(C_6H_5)_4SbF$ (methanolic solution) spectrum at 208 and 182 cm^{-1}, respectively, but not in the spectrum of the corresponding solution of the chloride salt are associated with the existence of a five-coordinate moiety, and an Sb–F stretch is observed at *ca.* 405 cm^{-1}. Similar modes are measured in these positions in the Raman spectra of the pentacoordinate antimony compounds in the solid state (see above) and are not found in the spectrum of tetraphenylantimony perchlorate.

The Raman spectra of aqueous solutions of the arsenic and antimony derivatives (Table III, Figures 3 and 4) are more difficult to interpret in structural terms. All the compounds included in the present study are known to be dissociated in an aqueous environment, and accurate osmotic and activity coefficients are available.[44] If species of coordination

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number greater than 4 are formed, this must be through direct hydration of the central atom. When reduced to a flat background through removal of the Rayleigh background, the laser-Raman spectra of the aqueous solutions of both the Sb(V) and As(V) ions contain at least five bands in the 200–300-cm^{-1} region. The occurrence of five peaks is independent of separation from the Rayleigh background and of curve resolution. The choice of background level and the details of curve resolution do have some effect on the relative intensities of the vibrations, however, and the illustrated resolution is that which we regard as providing the most accurate fit to the total curve envelope. The spectra are somewhat more complex than that of $(C_6H_5)_4SbCl$ in methanol, and they show greater similarity to that of methanolic $(C_6H_5)_4SbF$—an x fundamental occurs at *ca.* 195 cm^{-1}, and solvent broadening[29] may prevent resolution of additional low-frequency components of mode u from the strong polarized lines at 220 and 242 cm^{-1} in the spectra of Sb(V) and As(V) compounds, respectively. It thus seems possible that distortions from tetrahedral symmetry may occur through first-coordination-sphere hydration to form five-coordinate species in the aqueous solutions, although the evidence for this is not unambiguous.

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Substituted Fluorophosphine Base Adducts of Triborane(7) and Diborane(4)[1]

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Dimethylaminodifluorophosphine and difluorophosphine have been combined as the bases in adducts with triborane(7) and with diborane(4). These were made in sequential and essentially reversible reactions with tetraborane(10). The three new substances $[(CH_3)_2NPF_2]_2 \cdot B_2H_4$, $F_2PH \cdot B_3H_7$, and $(F_2PH)_2 \cdot B_2H_4$ have been characterized by analysis, mass spectrometry, infrared spectroscopy, and nmr. New data have been found for $(CH_3)_2NPF_2 \cdot B_3H_7$.

This paper reports the preparation of new acid–base derivatives of diborane(4) and some chemistry concerning adducts of triborane(7), namely, (1) their preparation from other triborane(7) adducts, (2) their transformation into diborane(4) adducts, and (3) their preparation from tetraborane(10).

Some bases (*e.g.*, PF_3 and CO) will not convert tetraborane to triborane(7) adducts; others (notably ethers and amines) do so with results for which the literature was summarized in a previous paper.[3] Of the triborane(7) adducts so formed some are subject to base displacement reactions, but at least two, $(CH_3)_3N \cdot B_3H_7$ and $(CH_3)_2O \cdot B_3H_7$, have been found to undergo borane adduct displacement by triphenylphosphine[4] and by trifluorophosphine,[3] respectively, with formation of diborane(4) adducts. Intuitively rather than deductively, the query arose whether there might be found bases of intermediate strength that would sequentially be the forming reagents with tetraborane(10) and the displacing reagents to give the diborane(4) adducts (*cf.* eq 1 and 2). Dimethylaminodifluorophosphine was known to give $(CH_3)_2NPF_2 \cdot B_3H_7$ from tetraborane(10)[5] under conditions so mild as to preclude further reaction, and the newly discovered difluorophosphine[6] seemed a similar substance. The speculation proved fruitful, since both the bases reacted with tetraborane(10) reversibly as described by the following equations, where b represents one of the bases

$$B_4H_{10} + 2b \rightleftharpoons b \cdot B_3H_7 + b \cdot BH_3 \qquad (1)$$

$$b \cdot B_3H_7 + 2b \rightleftharpoons b_2 \cdot B_2H_4 + b \cdot BH_3 \qquad (2)$$

Though one product in each forward reaction according to eq 2 was not diborane, but a borane adduct, diborane was used to accomplish the reversal. The best preparative method for the difluorophosphine adducts was not this process but one in which the first displacement reaction had dimethyl ether–triborane(7) as a reactant

$$(CH_3)_2O \cdot B_3H_7 + 2PF_2H \longrightarrow PF_2H \cdot B_3H_7 + (CH_3)_2O \qquad (3)$$

$$PF_2H \cdot B_3H_7 + 2PF_2H \longrightarrow (PF_2H)_2 \cdot B_2H_4 + PF_2H \cdot BH_3 \qquad (4)$$

The extent of reaction depended upon whether the reaction time was 30 sec or 4 min. The diborane(4) adducts reacted only slowly and incompletely with diborane (50% conversion), slowly with protic solvolytic reagents, and not at all with hydrogen. This is in contrast with the rapid reactions found for $(PF_3)_2 \cdot B_2H_4$. Considering the experience with the two phosphine bases, $(CH_3)_2NPF_2$ and PF_2H, it seems likely that failure to obtain $PF_3 \cdot B_3H_7$ must arise from its very great reactivity and from its inherent instability possibly with respect to the following reactions, two of them equilibria

$$B_4H_{10} + 2PF_3 \rightleftharpoons PF_3 \cdot B_3H_7 + F_3P \cdot BH_3 \qquad (5)$$

$$PF_3 \cdot B_3H_7 + 2PF_3 \rightleftharpoons (PF_3)_2 \cdot B_2H_4 + F_3P \cdot BH_3 \qquad (6)$$

$$2PF_3 \cdot B_3H_7 \longrightarrow (PF_3)_2 \cdot B_2H_4 + B_4H_{10} \qquad (7)$$

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