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Organoantimony Compounds. III.[1,2] Far-Infrared and Raman Spectroscopic Studies on Triorganoantimony(V) Derivatives, R_3SbX_2

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The infrared and Raman spectra (600–100 cm^{-1}) are reported for the series R_3SbX_2 (R = CH_3, C_6H_5; X = F, Cl, Br, NCS, ONO_2, CH_3COO, and CD_3COO). Assignments are made with particular emphasis on the Sb–C and Sb–X stretching vibrations. To aid in these assignments approximate normal-coordinate calculations were performed on $(CH_3)_3SbF_2$, $(CH_3)_3SbCl_2$, and $(CH_3)_3SbBr_2$, assuming the methyl groups to be single atoms and using a modified Urey–Bradley force field. Using previously reported vibrational data similar calculations were also performed on $SbCl_5$, $(CH_3)_5Sb$, and $(CH_3)_3Sb^{2+}$. The force constants obtained from these calculations are used to discuss the relative strengths of the Sb–C and Sb–X bonds.

Introduction

Infrared spectroscopy and X-ray diffraction methods have been used to elucidate the structures of R_3SbX_2 organoantimony derivatives. A trigonal-bipyramidal structure in which the antimony and methyl carbon atoms are coplanar and the halogen atoms are in the axial positions has been established for trimethylantimony dichloride, dibromide, and diiodide.[3] Crystallographic studies have shown a similar structure for triphenylantimony dichloride.[4] Recently infrared spectroscopic studies on the trimethyl- and triphenylantimony difluorides,[5,6] dinitrates,[5–7] diacetates,[6,7] and dipseudohalides[8] have indicated trigonal-bipyramidal structures for these compounds. Until the present, however, relatively few data have been available for the Sb–C and Sb–X stretching and bending vibrations for these compounds. We have investigated the far-infrared (600–100 cm^{-1}) and Raman spectra (600–100 cm^{-1}) of several R_3SbX_2 derivatives (R = CH_3, C_6H_5; X = F, Cl, Br, ONO_2, CH_3COO, CD_3COO, NCS). To aid in the assignment of these spectra, approximate normal-coordinate analyses have been carried out on trimethylantimony difluoride, dichloride, and dibromide using a modified Urey–Bradley force field.[9] A preliminary report of these results has been published.[10]

Experimental Section

Preparation of Compounds.—Trimethylantimony was prepared by the method of Morgan and Davies.[11] Triphenylantimony was obtained from Organometallics, Inc., and recrystallized successively from ethanol, carbon tetrachloride, and a mixture of chloroform and petroleum ether (bp 35–60°). The dihalides,[5,6] dinitrates,[5] and diisothiocyanates[8] were prepared using previously reported procedures. The diacetates and their deuterated analogs were prepared by the metathetical reaction between trimethyl- or triphenylantimony dibromide and silver acetate in methanol or benzene and recrystallized from hot petroleum ether (bp 35–60). Deuterated silver acetate was prepared by dissolving silver oxide in CD_3COOD, followed by recrystallization under reduced pressure. The crystals were washed with benzene and dried under vacuum. The purity of all compounds was established by carbon and hydrogen analyses and comparison with previously reported infrared spectra[5–8] and melting points.[6–8]

Spectral Measurements.—The infrared spectra were recorded on a Beckman IR-12 spectrophotometer (600–250 cm^{-1}) and a Hitachi Perkin-Elmer FIS-3 spectrophotometer (350–100 cm^{-1}). Both were calibrated using polyethylene film and water vapor. The samples were prepared as Nujol mulls on polyethylene or CsI plates. The frequencies are accurate to ±2 cm^{-1}. The Raman spectra were recorded on a Spex-Ramalog spectrophotometer equipped with an argon ion laser source. The spectra were measured on powdered samples in glass capillary tubes and have an accuracy of ±2 cm^{-1}.

Representative infrared spectra are presented in Figures 1 (600–200 cm^{-1}) and 2 (250–100 cm^{-1}) for $(CH_3)_3SbF_2$, $(CH_3)_3SbCl_2$, and $(CH_3)_3SbBr_2$, while Figure 3 presents the Raman spectra (600–100 cm^{-1}) for the same three compounds.

Procedure of Calculation

Assuming the methyl groups to be single atoms of mass 15, the molecules $(CH_3)_3SbX_2$ (X = F, Cl, Br) have a local symmetry of D_{3h}. Figure 4 illustrates the molecular model and internal coordinates used to express the potential energy. The representation for the normal vibrations of a D_{3h} $(CH_3)_3SbX_2$ structure is $\Gamma_{vib} = 2\,A_1' + 2\,A_2'' + 3\,E' + E''$ and the 14 internal coordinates used lead to two redundancies of A_1' symmetry. (Table I gives symmetry coordinates for the R_3MX_2 molecule.)

A Urey–Bradley force field,[12] modified with an angle–angle interaction force constant[9] was used in the calculation.

The potential energy was given by eq 1. The quan-

$$
\begin{aligned}
2V = {} & \sum_{i=1}^{3}[2K'_{\mathrm{M-R}}r(\Delta r_i) + K_{\mathrm{M-R}}(\Delta r_i)^2] + \\
& \sum_{i=1}^{2}[2K'_{\mathrm{M-X}}d(\Delta d_i) + K_{\mathrm{M-X}}(\Delta d_i)^2] + \\
& \sum_{i<j}[2H'_{\alpha}r_{\alpha}^2(\Delta\alpha_{ij}) + H_{\alpha}(r_{\alpha}\Delta\alpha_{ij})^2] + \\
& \sum_{i<j}[2H'_{\beta}r_{\beta}^2(\Delta\beta_{ij}) + H_{\beta}(r_{\beta}\Delta\beta_{ij})^2] + \\
& \sum_{i<j}[2F'_{\mathrm{RR}}q_{rr}(\Delta q_{ij}) + F_{\mathrm{RR}}(\Delta q_{ij})^2] + \\
& \sum_{k<j}[2F'_{\mathrm{RX}}q_{dr}(\Delta q_{jk}) + F_{\mathrm{RX}}(\Delta q_{jk})^2] + \\
& \sum_{k\neq i<j}2H_{\alpha\beta}(r_{\alpha}\Delta\alpha_{ij})(r_{\beta}\Delta\beta_{ik})
\end{aligned}
\quad (1)
$$

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(1) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

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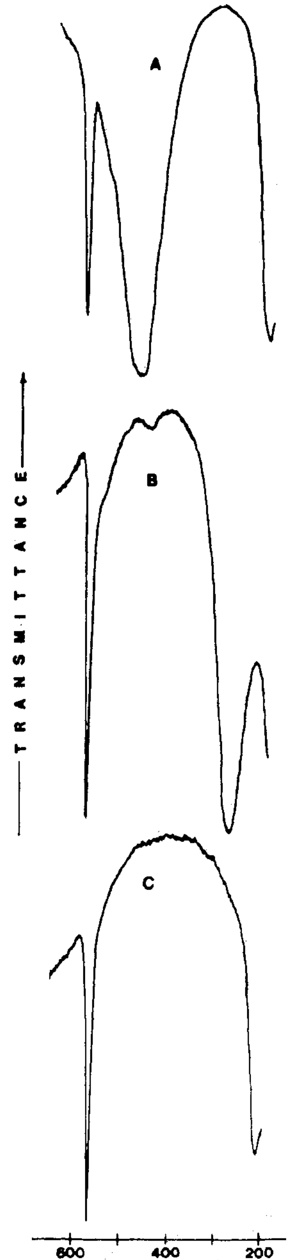

Figure 1.—Infrared spectra (600–200 cm^{-1}) of (A) $(CH_3)_3SbF_2$, (B) $(CH_3)_3SbCl_2$, and (C) $(CH_3)_3SbBr_2$.

tities K' and H' vanish since they can be expressed in terms of F'. F' was taken as $-0.1F$ by making the usual assumption that the repulsive energy between the nonbonded atoms is proportional to r^{-6}.

A matrix equation of the form $|GF - E\lambda| = 0$ was constructed for each species and solved by using an IBM 360/50 computer. In addition to calculating the skeletal modes for the series $(CH_3)_3SbX_2$ (X = F, Cl, Br) previously reported vibrational data were used to perform similar calculations on $SbCl_5$,[9] $(CH_3)_3PF_2$,[13] PF_5,[14] $(CH_3)_3Sb^{2+}$,[15] and $(CH_3)_5Sb$.[16]

TABLE I

SYMMETRY COORDINATES IN THE R_3MX_2 MOLECULE

	Sym	Type
$S_1 = (1/\sqrt{3})[\Delta r_1 + \Delta r_2 + \Delta r_3]$	A_1'	ν_s(M–R)
$S_2 = (1/\sqrt{2})[\Delta d_1 + \Delta d_2]$	A_1'	ν_s(M–X)
$S_3 = 1/\sqrt{3}[\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{13}]$	A_1'	Redun
$S_4 = 1/\sqrt{6}[\Delta\beta_{15} + \Delta\beta_{25} + \Delta\beta_{35} + \Delta\beta_{14} + \Delta\beta_{24} + \Delta\beta_{34}]$	A_1'	Redun
$S_5 = (1/\sqrt{2})[\Delta d_1 - \Delta d_2]$	A_2''	ν_a(M–X)
$S_6 = (1/\sqrt{6})[\Delta\beta_{15} + \Delta\beta_{25} + \Delta\beta_{35} - \Delta\beta_{14} - \Delta\beta_{24} - \Delta\beta_{34}]$	A_2''	$\delta_\perp$(M–R)
$S_{7A} = (1/\sqrt{6})[2\Delta r_1 - \Delta r_2 - \Delta r_3]$	E_A'	ν_a(M–R)
$S_{7B} = (1/\sqrt{2})[\Delta r_2 - \Delta r_3]$	E_B'	ν_a(M–R)
$S_{8A} = (1/\sqrt{6})[2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{13}]$	E_A'	$\delta_\|$(M–R)
$S_{8B} = (1/\sqrt{2})[\Delta\alpha_{13} - \Delta\alpha_{12}]$	E_B'	$\delta_\|$(M–R)
$S_{9A} = (1/\sqrt{12})[2\Delta\beta_{15} - \Delta\beta_{25} - \Delta\beta_{35} + 2\Delta\beta_{14} - \Delta\beta_{24} - \Delta\beta_{34}]$	E_A'	δ(M–X)
$S_{9B} = (1/2)[\Delta\beta_{25} - \Delta\beta_{35} + \Delta\beta_{24} - \Delta\beta_{34}]$	E_B'	δ(M–X)
$S_{10A} = (1/\sqrt{12})[2\Delta\beta_{15} - \Delta\beta_{25} - \Delta\beta_{35} - 2\Delta\beta_{14} + \Delta\beta_{24} + \Delta\beta_{34}]$	E_A''	$\rho_r(MR_3X_2)$
$S_{10B} = (1/2)[\Delta\beta_{25} - \Delta\beta_{35} - \Delta\beta_{24} + \Delta\beta_{34}]$	E_B''	$\rho_r(MR_3X_2)$

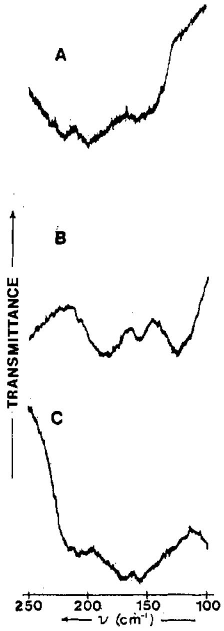

Figure 2.—Infrared spectra (250–100 cm^{-1}) of (A) $(CH_3)_3SbF_2$, (B) $(CH_3)_3SbCl_2$, and (C) $(CH_3)_3SbBr_2$.

The force constants for $SbCl_5$ and PF_5 were taken from a previous calculation[9] and adjusted to fit the latest vibrational assignments. For $(CH_3)_3Sb^{2+}$, trial values of K(Sb–R), H(R–Sb–R), and F(R···R) were estimated from previous calculations on other organometallic compounds.[17,18] They were then adjusted to give the best fit for the three observed bands. The values of K(Sb–R), H(R–Sb–R), and F(R···R) obtained for $(CH_3)_3Sb^{2+}$ were transferred to $(CH_3)_5Sb$ and the series $(CH_3)_3SbX_2$ (X = F, Cl, Br). Reasonable estimates were then made for the remaining force constants. The value of F(R···R) was constrained to that obtained for $(CH_3)_3Sb^{2+}$. Since $H_{\alpha\beta}$ did not improve the results for the series $(CH_3)_3SbX_2$ (X = F, Cl, Br) it was constrained to zero. The force constants used for $(CH_3)_3PF_2$ were chosen in a similar manner to that described above.

The bond lengths and angles used are listed in Table

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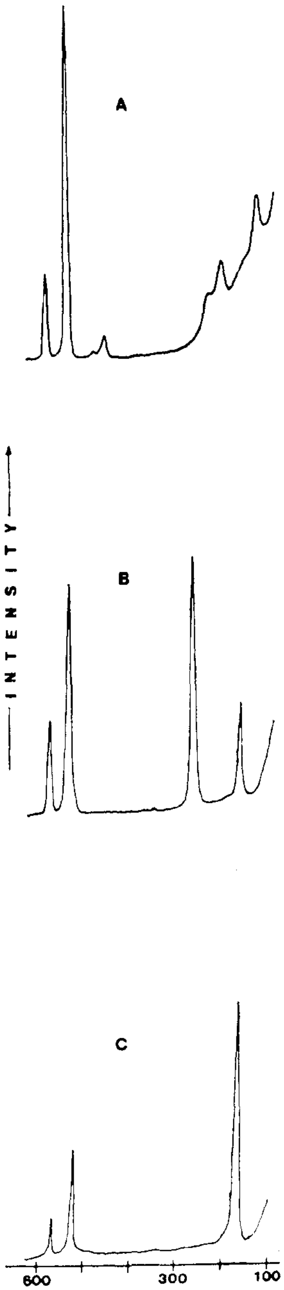

Figure 3.—Raman spectra (600–100 cm^{-1}) of (A) $(CH_3)_3SbF_2$, (B) $(CH_3)_3SbCl_2$, and (C) $(CH_3)_3SbBr_2$.

II.[3,13,19,20] The best set of force constants obtained for the antimony compounds is listed in Table III. Table IV compares the observed frequencies for these compounds with those calculated using these sets of force constants. The potential energy distribution for the series $(CH_3)_3SbX_2$ (X = F, Cl, Br) is shown in Table V.

Results and Discussion

Vibrational Assignments.—The assignment of the skeletal vibrations for the series R_3SbX_2 (R = CH_3, C_6H_5; X = F, Cl, Br, ONO_2, CH_3COO, NCS) is divided into two sections. The first deals with the methyl compounds and the second with the phenyl compounds.

Methyl Compounds.—The infrared and Raman spectra for all of the methyl compounds are very similar.

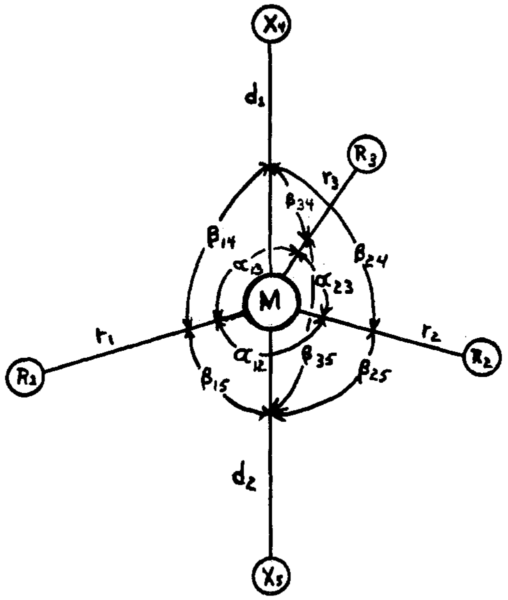

Figure 4.—Structure and internal coordinates of a trigonal-bipyramidal R_3MX_2 molecule.

TABLE II

MOLECULAR PARAMETERS[a]

Compd	Bond	Length, Å
$(CH_3)_3SbF_2$	Sb–F[b]	2.14
	Sb–C[c]	2.15
$(CH_3)_3SbCl_2$	Sb–Cl[d]	2.53
	Sb–C[d]	2.15
$(CH_3)_3SbBr_2$	Sb–Br[d]	2.63
	Sb–C[d]	2.15
$(CH_3)_5Sb$, $(CH_3)_3Sb_{aq}{}^{2+}$	Sb–C[e]	2.15
$SbCl_5$	Sb–Cl_{axial}[f]	2.43
	Sb–Cl_{eq}[f]	2.31
$(CH_3)_3PF_2$	P–F[g]	1.68
	P–C[g]	1.80
PF_5	P–F_{axial}[h]	1.577
	P–F_{eq}[h]	1.534

[a] R–M–R = 120°; R–M–X = 90°. [b] [2.37 (av of Sb–Cl in $SbCl_5$)]/[2.53 (Sb–Cl in $(CH_3)_3SbCl_2$)] = [~2.00 (av SbF in SbF_5)]/[x (Sb–F in $(CH_3)_3SbF_2$)]. [c] Taken to be the same as Sb–C in $(CH_3)_3SbCl_2$. [d] Reference 3. [e] Average Sb–C taken to be the same as Sb–C in $(CH_3)_3SbCl_2$. [f] Reference 19. [g] Reference 13. [h] Reference 20.

Figures 1–3 illustrate the basic features observed for all members of this series. The assignments for the methyl compounds are presented in Table VI. The asymmetric Sb–CH_3 stretching mode (ν_a(Sb–CH_3)) appears as a strong band in the infrared spectrum and as a medium-intensity band in the Raman spectrum at *ca.* 570–590 cm^{-1}. For D_{3h} symmetry the ν_s(Sb–CH_3) mode is expected to be only Raman active. It is observed as a very strong band between 550 and 525 cm^{-1} in the Raman spectra but is absent in the infrared spectra. Therefore, the methyl carbon atoms and antimony atom are coplanar for the methyl series.

The ν_a(Sb–F) mode is observed as a strong infrared band at 480 cm^{-1}, while the ν_s(Sb–F) mode is observed as a weak Raman band at 465 cm^{-1}. The ν_a(Sb–Cl) mode appears at 280 cm^{-1} and the ν_s(Sb–Cl) mode at 272 cm^{-1}. The ν_a(Sb–Br) mode is not as readily assigned. The ν(Sb–Br) modes have been assigned between 250 and 222 cm^{-1} for $SbBr_3$.[21–23] One would ex-

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TABLE III

UREY–BRADLEY FORCE CONSTANTS (MDYN/Å) FOR R_3MX_2 TYPE MOLECULES

	K(M–R)	K(M–X)	$H\alpha$(R–M–X)	$H\beta$(R–M–X)	F(R···R)	F(R···X)	$H\alpha\beta$
$(CH_3)_3Sb_{aq}{}^{2+}$	2.44	...	0.053	...	0.054	...	...
$(CH_3)_3SbF_2$	2.39	2.02	0.053	0.109	0.054[a]	0.145	0.00[a]
$(CH_3)_3SbCl_2$	2.35	1.11	0.045	0.067	0.054[a]	0.109	0.00[a]
$(CH_3)_3SbBr_2$	2.29	0.94	0.043	0.054	0.054[a]	0.087	0.00[a]
$(CH_3)_5Sb$	1.90	1.40	0.034	0.096	0.054[a]	0.087	0.025
$SbCl_5$	2.15	1.80	0.057	0.080	0.090	0.132	0.042

[a] Constrained.

TABLE IV

OBSERVED AND CALCULATED FREQUENCIES (CM^{-1}) FOR SEVERAL TRIGONAL-BIPYRAMIDAL ANTIMONY COMPOUNDS

Principal		$SbCl_5$		$(CH_3)_3Sb_{aq}{}^{2+}$		$(CH_3)_3SbF_2$		$(CH_3)_3SbCl_2$		$(CH_3)_3SbBr_2$		$(CH_3)_5Sb$	
contribution[a]	Species	Calcd	Obsd[9]	Calcd	Obsd[15]	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd[16]
ν_s(MR)	A_1'	354	356	542	536	554	546	541	538	533	527	494	493
ν_s(MX)	A_1'	307	307	...	...	441	465	249	272	152	169	411	414
ν_a(MX)	A_2''	383	380 387	...	...	503	480	305	280	229	212	458	456
$\delta_\perp$(MR)	A_2''	154	154	...	...	233	220	204	188	178	170	205	213
ν_a(MR)	E′	400	398	574	582	581	590	572	580	563	570	517	516
$\delta_{\|\|}$(MR)	E′	74	74	166	166	156	158	159	158	156	156	109	108
δ(MX)	E′	172	172	...	...	188	200	103	126	95	*b*	202	195
$\rho_r(MR_3X_2)$	E″	162	165	...	...	261	245	203	173	175	*b*	236	239

[a] Description of abbreviations: ν, stretching; δ, bending; $\delta_\perp$, out-of-plane bending; $\delta_{||}$, in-plane bending; ρ_r, rocking; s, symmetric; a, asymmetric. [b] Not observed.

TABLE V

POTENTIAL ENERGY DISTRIBUTION FOR THE SERIES $(CH_3)_3SbX_2$ (X = F, Cl, Br)

A_1' Species

Sym	Obsd freq, cm^{-1}					
coord	546	465	538	272	527	169
	$(CH_3)_3SbF_2$		$(CH_3)_3SbCl_2$		$(CH_3)_3SbBr_2$	
S_1	1.00	0.00	1.00	0.00	1.00	0.00
S_2	0.00	1.00	0.00	1.00	0.00	1.00

A_2'' Species

	Obsd freq, cm^{-1}					
Sym	480	220	280	188	212	170
coord	$(CH_3)_3SbF_2$		$(CH_3)_3SbCl_2$		$(CH_3)_3SbBr_2$	
S_5	1.00	0.00	1.00	0.00	1.00	0.29
S_6	0.00	1.00	0.00	1.00	0.07	1.00

E′ Species

	Obsd freq, cm^{-1}								
Sym	590	200	158	580	158	126	580	156	95[a]
coord	$(CH_3)_3SbF_2$			$(CH_3)_3SbCl_2$			$(CH_3)_3SbBr_2$		
S_7	1.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00
S_8	0.00	0.44	1.00	0.00	0.10	0.00	0.00	1.00	0.00
S_9	0.00	1.00	0.43	0.00	0.00	1.00	0.00	0.00	1.00

[a] Calculated frequency.

pect the ν(Sb–Br) modes for $(CH_3)_3SbBr_2$ to occur at lower frequencies than in $SbBr_3$ as is the case when the ν(Sb–Cl) modes of $SbCl_3$[21] are compared with those of $(CH_3)_3SbCl_2$. A very strong Raman band for $(CH_3)_3SbBr_2$ at 169 cm^{-1} is assigned to the ν_s(Sb–Br) mode since no other bands are present which could be assigned to this mode. The assignment of ν_a(Sb–Br) is complicated by the presence of two infrared bands which could be assigned to this mode. One band occurs at 212 cm^{-1} and the other at 170 cm^{-1}. The out-of-plane Sb–C bending mode ($\delta_\perp$(Sb–C)) is expected to be in the same region and to have the same symmetry (A_2'') as the ν_a(Sb–Br) mode. Since both modes are in the same region and are also of the same symmetry, coupling is possible. The normal-coordinate calculations show this to be the case. The 212-cm^{-1} band is assigned to the ν_a(Sb–Br) mode, and the 170-cm^{-1} band, to the $\delta_\perp$(Sb–C) mode. The $\nu_a(Sb–ONO_2)$ and ν_a(Sb–NCS) modes appear at 280 and 268 cm^{-1}, respectively. The ν_a(Sb–O) mode of $(CH_3)_3Sb(CH_3COO)_2$ is assigned at 279 cm^{-1} and is observed to shift to 268 cm^{-1} on deuterating the acetate groups. The $\delta_\perp$(Sb–C) modes for all of the methyl compounds show a variation in position. This perhaps can be attributed to the steric effect of the axial groups. The in-plane Sb–C bending modes ($\delta_{||}$(Sb–C)), however, appear at approximately the same position in all of the methyl compounds. Recently, there has been some disagreement as to the assignment of the $\delta(MX_{eq})$ and $\delta(MX_{axial})$ modes in MX_5 trigonal-bipyramidal compounds.[14,24,25] This will be considered when the normal-coordinate calculations are discussed (*vide infra*). The Raman-active $\rho_r(MR_3X_2)$ mode is also assigned.

Phenyl Compounds.—The vibrational spectra of the $(C_6H_5)_3SbX_2$ compounds are more complex than those of the corresponding methyl derivatives. The assignments for the phenyl compounds have been made by comparing their spectra with those of the corresponding methyl compounds and with the recent assignments made for $(C_6H_5)_3Sb$.[26] Therefore, rather than speaking of pure Sb–C modes, reference will be made to metal- or "X-sensitive" vibrations.[27]

The stretching of the phenyl–metal bond contributes to three of the six "X-sensitive" vibrations (the q, r, and t modes). It has been suggested that while for light elements the major contribution of the ν(M–C) mode may be to the q vibration;[28] for heavier elements such as Ge, As, and Sb it is to the t vibration.[29] Therefore, the t mode will loosely be referred to as the ν(Sb–C) vibration. In the triphenylantimony compounds the t mode consists of two bands, both of which are infrared and Raman active. A local symmetry of D_{3h} for the trimethylantimony compounds permits only one infrared-active ν(Sb–C) mode. The infrared activity of both phenyl "ν(Sb–C)" modes can be attributed in part to a

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TABLE VI

VIBRATIONAL SPECTRA (600–100 CM^{-1}) OF $(CH_3)_3SbX_2$ SERIES[a]

	$(CH_3)_3SbF_2$		$(CH_3)_3SbCl_2$		$(CH_3)_3SbBr_2$		$(CH_3)_3Sb(ONO_2)_2$		$(CH_3)_3Sb(NCS)_2$		$(CH_3)_3Sb(CH_3COO)_2$	
Description	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R
ν_a(Sb–C)	590 vs	591 m	580 vs	580 m	570 vs	570 m	582 s	586 m	584 s	585 m	578 vs	578 m
ν_s(Sb–C)		546 vs		538 vs		527 vs		535 vs		535 vs		538 vs
											507 vs	512 w
ν_a(Sb–F)	480 vs											
ν_s(Sb–F)		462 w										
δ_a(NCS)									492 s	492 w		
δ_s(NCS)									482 m	483 vw		
ν_a(Sb–Cl)			280 vs									
ν_s(Sb–Cl)				272 vs								
ν_a(Sb–O)							275 vs				279 vs	
ν_s(Sb–O)								273 w				275 vs
ν_a(Sb–N)									268 vs			
ν_s(Sb–N)												
		245 m						238 w		194 m	218 m	223 m
ν_a(Sb–Br)					212 s							
ν_s(Sb–Br)						169 vs						
$\delta_\perp$(Sb–C)	220 vs	220 m	188 vs		170 vs		202 s		180 s		212 s	
				173 m				163 w				168 m
$\delta_{\|\|}$(Sb–C)	158 m		158 m		156 s		156 s		152 m		156 m	
δ(Sb–X)	200 vs	145 m	126 s				128 s				128 s	125 m

[a] Key: vs, very strong; vw, very weak; s, strong; w, weak; m, medium; ν_a, asymmetric stretch; ν_s, symmetric stretch; δ, out-of-plane bend; $\delta_{||}$, in-plane bend; ir, infrared; R, Raman.

TABLE VII

VIBRATIONAL SPECTRA (600–100 CM^{-1}) OF $(C_6H_5)_3SbX_2$ SERIES[a]

	$(C_6H_5)_3SbF_2$		$(C_6H_5)_3SbCl_2$		$(C_6H_5)_3SbBr_2$		$(C_6H_5)_3Sb(ONO_2)_2$		$(C_6H_5)_3Sb(NCS)_2$		$(C_6H_5)_3Sb(CH_3COO)_2$	
Description	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R
											540 vs	
ν_a(Sb–F)	509 vs											
ν_s(Sb–F)	491 w	485 s										
δ_a(NCS)									496 w	496 s		
δ_s(NCS)									480 m	486 m		
y vibration	485 vs	458 m	457 vs	457 w	456 vs	457 w	460 vs		455 vs	455 w	461 vs	461 m
w vibration				400 vw		400 vw				400 vw		
t vibration	292 vs	288 m	288 vs[b]		294 vs	293 m	295 vs		294 vs[b]		306 vs	305 m
ν_a(Sb–O)							275 vs				288 vs	
ν_s(Sb–O)								272 s				287 s
ν_s(Sb–Cl)				275 vs								
t vibration	244 m	255 s	255 m	255 m	248 s		242 m		254 m	264 m		265 vs
											237 s	235 s
	234 m											
			234 w				225 w		230 w			
x vibration		222 vs	212 m	214 s		219 s	214 m	216 vs		219 vs	216 w	219 vs
δ(Sb–X) and δ(Sb–C)							198 m					
δ(Sb–X) and δ(Sb–C)			192 m						187 m			
δ(Sb–X) and δ(Sb–C)							180 w					
ν_a(Sb–Br)					188 vs							
ν_s(Sb–Br)						161 vs						
u vibration	158 w		162 m		162 w		158 w		160 w		150 m	150 m
			151 m				140 m				136 m	
			122 w								126 m	

[a] Key: vs, very strong; vw, very weak; s, strong; w, weak; m, medium; ν_a, asymmetric stretch; ν_s, symmetric stretch; δ, bend; ir, infrared; R, Raman. [b] Band overlaps ν_a(Sb–X) vibration.

breakdown of the local symmetry approximation due to the coupling of the Sb–C and phenyl ring vibrations. Table VII lists the assignments made for the phenyl compounds.

The metal-sensitive antimony–phenyl vibrations found in $(C_6H_5)_3Sb$ are also observed for the $(C_6H_5)_3SbX_2$ series. The only vibrational mode which is shifted is the higher component of the t vibration, which is found at 270 cm^{-1} in $(C_6H_5)_3Sb$ but at *ca.* 295 cm^{-1} in the $(C_6H_5)_3SbX_2$ series.

The ν(Sb–F) modes occur at higher frequencies in the phenyl compounds than in the methyl compound. The ν_a(Sb–X) modes for $(C_6H_5)_3SbCl_2$ and $(C_6H_5)_3Sb(NCS)_2$ are obscured in the infrared spectra by the higher component of the t mode which occurs at *ca.* 295 cm^{-1}. The ν_a(Sb–O) mode for $(C_6H_5)_3Sb(ONO_2)_2$ appears at 275 cm^{-1}, corresponding to the value found for $(CH_3)_3Sb(ONO_2)_2$. As seen in Figure 5, two bands (at 306 and 288 cm^{-1}) appear in the region expected for the ν_a(Sb–O) mode of $(C_6H_5)_3Sb(CH_3COO)_2$. On deuterating the acetate group, the 288-cm^{-1} band shifts to 277 cm^{-1} but the 306-cm^{-1} band remains unchanged. The 288-cm^{-1} band is therefore assigned to the ν_a(Sb–O) mode. The ν_a(Sb–Br) mode for $(C_6H_5)_3SbBr_2$ appears at approximately the same position as was observed for the methyl compound. The ν_a(Sb–Br) mode, however, is at lower frequency in $(C_6H_5)_3SbBr_2$ than in $(CH_3)_3SbBr_2$. This might be accounted for by the absence of coupling between the ν_a(Sb–Br) and $\delta_\perp$(Sb–C) modes in the phenyl compound.

Force Constants.—Several trends are observed in the force constants obtained for the methyl halides

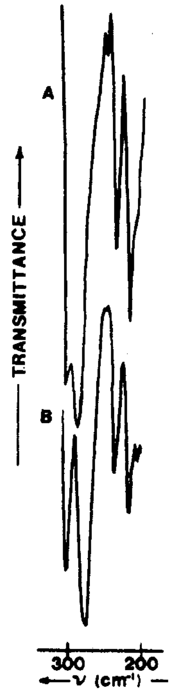

Figure 5.—Infrared spectra (300–200 cm^{-1}) of (A) $(CH_3)_3Sb(CH_3COO)_2$ and (B) $(CH_3)_3Sb(CD_3COO)_2$.

(Table III). The equatorial Sb–C stretching force constant decreases slightly in the order $(CH_3)_3Sb_{aq}{}^{2+} > (CH_3)_3SbF_2 > (CH_3)_3SbCl_2 > (CH_3)_3SbBr_2 > (CH_3)_5Sb$, indicating the strengthening of the equatorial Sb–C bond with an increase in the positive charge on the antimony atom. Although this trend might have resulted from the approximations used in the calculations, it is noted that a similar trend has been reported for the Sn–C stretching force constant in the series $K_2[(CH_3)_2SnX_4]$[30] (X = F, Cl, Br).

The weakening of the antimony–halogen bond by the methyl groups is also evident when the axial Sb–Cl stretching force constants in $(CH_3)_3SbCl_2$ and $SbCl_5$ are compared (Table VIII). Table VIII also includes a comparison of the relative strength of these two Sb–Cl bonds using Pauling's relationship.[31] A similar effect has been noted for the series $(CH_3)_nPF_{5-n}$ ($n = 3$).[13] We have included, for comparison, our values for the axial P–F stretching force constants for $(CH_3)_3PF_2$ and PF_5 in Table VIII. Although the methyl groups weaken the axial antimony–halogen bonds, the force constants indicate that the antimony–halogen bonds still retain considerable covalent character.

TABLE VIII
RELATIVE Sb–Cl AND P–F BOND ORDERS

Compd	Pauling's relation[a]	Urey–Bradley force const
$SbCl_5$	1.00	1.00
$(CH_3)_3SbCl_2$	0.68	0.62
PF_5	1.00	1.00
$(CH_3)_3PF_2$	0.69	0.58

[a] $D_{(n)} = D_{(1)} - 0.60 \log n$, where $D_{(n)}$ is bond length of order n and $n < 1$.

Mention was made earlier of the controversy concerning the assignment of the two E′ bending modes of MX_5 trigonal-bipyramidal molecules. We believe that the discussion of Bartell[24] strongly supports the assignment of the higher frequency to the axial bending mode. We have, therefore, reversed the original assignments made for the two E′ bending modes in $SbCl_5$[9] and $(CH_3)_5Sb$[16] (Table IV). As Bartell has pointed out, the relative weakness of the axial bonds compared to the equatorial bonds is not a valid basis on which to conclude that the axial bending mode is of lower frequency than the equatorial bending mode. Rather than comparing stretching force constants (which have been empirically related to bond strength) it seems more appropriate to compare bending force constants. The Urey–Bradley bending and repulsive force constants for the two MX_5 compounds we have examined ($SbCl_5$ and $(CH_3)_5Sb$) lend support to Bartell's argument. The X_{axial}–M–X_{eq} bending and repulsive force constants are larger than the X_{eq}–M–X_{eq} bending and repulsive force constants. This indicates that the axial bending and δ bending modes would encounter more resistance than the $\delta_{||}$ modes and might therefore be expected at a higher frequency. Bartell also indicated that strong coupling might be expected between these two E′ bending modes. Holmes and Golen[25] concluded that this is the case for PF_5. Therefore, it seems more valid to refer to highly coupled modes rather than to try to distinguish between the different bending vibrations.

It has also been suggested that the two E′ bending modes make up the intermolecular exchange coordinate for a pseudorotation process.[9] The introduction of the angle–angle interaction force constant, $H_{\alpha\beta}$, into the Urey–Bradley force field was justified because of the possibility of pseudorotation in the MX_5 systems studied.[9] It is necessary to include this force constant to fit the calculated and observed MX_5 E′ bending frequencies. This particular force constant, however, is essentially zero in the $(CH_3)_3SbX_2$ series. This is interpreted as indicating that pseudorotation is much less likely to occur in this series.

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