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Arsenites and Antimonites. II. Vibrational, Nuclear Quadrupole Resonance, and Mass Spectral Properties of Arsenic(III) and Antimony(III) Esters and Thioesters[1]

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Twenty-four symmetric trivalent arsenites, antimonites, thioarsenites, and thioantimonites having the general stoichiometry $E(YR)_3$ (where E = As, Sb; Y = O, S; R = typical alkyl and aryl groups) have been prepared using known procedures. The ir and Raman spectra reveal that the EO-R stretching vibrations lie in the 995-1180-cm^{-1} region and by comparison to the analogous phosphite spectra are invariant to whether E = P, As, or Sb. On the other hand, the symmetric and antisymmetric E-OR stretching motion is E dependent and lies at 575-699 cm^{-1} when E = As and 540-612 cm^{-1} when E = Sb. This compares with 730-875 cm^{-1} when E = P. The E-OR bending motions lie at 328-394 cm^{-1} for E = As and 310-380 cm^{-1} for E = Sb. The ES-R stretching motion falls in the 610-790-cm^{-1} range for E = As and Sb and is fairly independent of E. The symmetric and antisymmetric E-SR stretching modes lie at 345-437 cm^{-1} when E = As and 338-400 cm^{-1} when E = Sb. The analogous P-SR motion occurs at 500-620 cm^{-1}. The As-SR bending modes lie in the 230-296-cm^{-1} region in the compounds studied. For motions involving the EY_3 skeleton the expected and observed trend in the vibrational frequencies is E = P > As > Sb. The mass spectral fragmentation pattern for the compounds is presented. The most intense ion is usually $E(YR)_2^+$. In some cases, however, rearrangement decomposition involving the loss of one or more hydrogen atoms results in unusual and very intense species. In the case of the phenyl derivatives, these ions may be ortho-metalated fragments. The ^{75}As, ^{121}Sb, ^{123}Sb, and ^{35}Cl nuclear quadrupole resonance spectra of several of the compounds are presented.

Introduction

The spectroscopic behavior of alkyl and aryl esters of phosphorus(III), $P(OR)_3$, is well known primarily because of their reasonable stability, availability, and extensive use as ligands toward transition metal elements. They also have found industrial application as catalysts and stabilizers in polymer systems which has solidified their importance. The thio homologs of these compounds are less well studied. The analogous arsenic and antimony compounds have, however, received comparatively little attention. The alkoxides and thioalkoxides of arsenic and antimony are known to be catalysts in a number of types of polymerization reactions and to have fungicidal and insecticidal activity. In spite of these applications surprisingly little is known about their systematic spectroscopic properties, perhaps principally because they have not yet found extensive use as ligands in transition metal systems. Several papers do report their use as ligands but the work mostly has been restricted to arsenites.[1,2]

Experimental Section

Materials and General Information. Alcohols and thiols were purchased from Matheson Coleman and Bell and Eastman Organics and were used without further purification. All solvents were dried over Linde 5A molecular sieves. $AsCl_3$ and $SbCl_3$ were obtained from Research Organic-Research Inorganic Chemicals. Glassware was heated in an oven to 100° before use. Dry N_2 was employed as an atmosphere during all synthetic manipulations. Solvents were degassed using N_2 before use. Analyses were carried out by Chemalytics, Tempe, Ariz., and Micro-Analysis, Inc., Wilmington, Del.

Syntheses. A number of procedures have been developed over the years for the preparation of the compounds used in this study, and we have used variations on some of the more routine ones.[3,4]

$As(Or)_3$ ($R = C_2H_5, C_3H_7, CH(CH_3)_2, C_4H_9, C(CH_3)_3, C_6H_5, C_6H_4CH_3$); $As(SR)_3$ ($R = C_2H_5, C_3H_7, CH(CH_3)_2, C(CH_3)_3$). The appropriate alcohol or thiol (0.18 mol) was mixed with the appropriate solvent mentioned in Table I and was placed in a 500-ml, three-neck flask equipped with a stirring bar, reflux condenser, gas inlet tube, and dropping funnel. While stirring, $AsCl_3$ (0.06 mol) was added dropwise using the funnel. When this addition was complete, dry NH_3 gas (other bases, such as pyridine and *N,N*-dimethylaniline, may also be used) was passed through the solution until no more was absorbed. The NH_4Cl precipitate was then filtered off and the solvent removed from the filtrate using a "Roto Vap." The remaining product was multiply distilled under vacuum to yield the desired compound.

$As(OCH_3)_3$. In a 250-ml, two-neck flask $AsCl_3$ (0.12 mol) was mixed with absolute methanol (3.75 mol). The reaction vessel was placed in an ice bath and NH_3 gas was bubbled through the solution for a period of 1 hr. The NH_3 flow was discontinued and the solution allowed to sit at room temperature for 96 hr. The NH_4Cl precipitate which formed was filtered off and the filtrate was distilled slowly at atmospheric pressure to remove excess CH_3OH. The remaining liquid was then distilled under vacuum to yield colorless $As(OCH_3)_3$.

$As(SR)_3$ ($R = C_6H_5, C_6H_4CH_3, C_6H_4Cl$) and $Sb(SC_6H_5)_3$. The sodium salt of the aryl thiol was prepared by mixing sodium metal (0.18 mol) with absolute methanol (50 ml) containing the thiol (0.18 mol). This mixture was transferred to a two-neck flask equipped with a reflux condenser and a dropping funnel containing $AsCl_3$ or $SbCl_3$ (0.06 mol) dissolved in 100 ml of benzene. After adding the group Va halide dropwise, the reaction was stirred at 40° for 2 hr. At this time the solvent was removed using a Roto Vap and the product was extracted with 100 ml of warm benzene. The solution was filtered and evaporated again. The product formed was a solid and was recrystallized from absolute ethanol. This procedure proved to yield somewhat cleaner products when R = an aryl group than the NH_3 method.

$Sb(OR)_3$ ($R = C_2H_5, C_3H_7, CH(CH_3)_2, C_4H_9, C(CH_3)_3, C_6H_5$) and $Sb(SR)_3$ ($R = CH(CH_3)_2, C_4H_9$). $SbCl_3$ (0.66 mol) dissolved in the solvent listed in Table I was added to the appropriate alcohol or thiol (2.2 mol) in a two-neck flask equipped with a condenser and gas inlet tube. Dry NH_3 gas was passed through the solution until no more was absorbed. The NH_4Cl formed was filtered off and the solvent removed using a "Roto Vap." The products were purified by multiple distillation under vacuum.

Reaction of $AsCl_3$ and $SbCl_3$ with $NaSeC_6H_5$. Using the procedure described above for $NaSC_6H_5$, $NaSeC_6H_5$ was prepared and allowed to react with $AsCl_3$ and $SbCl_3$ dissolved in 100 ml of benzene in a 3:1 molar ratio. The NaCl was removed by filtration and yellow crystals formed upon evaporation of the filtrate. These were recrystallized from methanol; mp 61-62°. The mass spectrum revealed that the sample was diphenyl diselenide, $C_6H_5SeSeC_6H_5$. *Anal.* Calcd for $C_{12}H_{10}Se_2$: C, 45.45; H, 3.20. Found: C, 45.11; H, 3.31.

Physical Measurements. Ir spectra were measured on a Perkin-

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Table I. Analytical Data for $E(YR)_3$ Compounds

				% C		% H	
Compd	Solvent	Mp, °C	Bp, °C (mm)	Calcd	Found	Calcd	Found
$As(OCH_3)_3$			60 (10.0)	21.30	20.92	5.35	5.20
$As(OC_2H_5)_3$	250 ml of hexane		61 (4.0)	34.20	34.02	7.15	7.29
$As(OC_3H_7)_3$	250 ml of hexane		63 (4.0)	42.87	43.18	8.34	8.16
$As(OC_4H_9)_3$	250 ml of hexane		68–70 (0.03)	48.99	48.76	9.19	9.05
$As[OCH(CH_3)_2]_3$	250 ml of hexane		58 (10.0)	42.87	42.40	8.34	8.53
$As[OC(CH_3)_3]_3$	250 ml of hexane		27–28 (0.03)	48.99	49.23	9.19	9.27
$As(OC_6H_5)_3$	200 ml of xylene	34–35	160 (0.05)	61.03	60.70	4.24	4.35
$As(SC_2H_5)_3$	250 ml of benzene		122 (4.0)	27.91	28.35	5.81	5.94
$As(SC_3H_7)_3$	250 ml of benzene		129–130 (0.3)	36.09	36.30	7.00	7.11
$As[SCH(CH_3)_2]_3$	250 ml of benzene		126–127 (4.0)	36.09	36.74	7.00	7.35
$As[SC(CH_3)_3]_3$	250 ml of benzene		125 (0.1)	42.11	42.38	7.89	7.99
$As(SC_6H_5)_3$		94		53.74	53.94	3.73	4.00
$As(SC_6H_4CH_3)_3$		76		56.37	56.26	4.73	4.81
$Sb(OC_2H_5)_3$	200 ml of ethanol		37–38 (0.05)	28.04	27.64	5.84	5.63
$Sb(OC_3H_7)_3$	200 ml of 1-propanol		54–55 (0.05)	36.15	36.27	7.03	6.75
$Sb(OC_4H_9)_3$	200 ml of benzene		105 (1.0)	42.26	41.94	7.92	7.61
$Sb[OCH(CH_3)_2]_3$	200 ml of 2-propanol		29 (0.05)	36.15	36.45	7.03	7.23
$Sb[OC(CH_3)_3]_3$	200 ml of benzene		64 (1.0)	42.26	42.19	7.92	7.60
$Sb(SC_6H_5)_3$	100 ml of benzene	67–68		48.13	47.86	3.34	3.09

Elmer Model 180 double-beam grating spectrophotometer between 1500 and 200 cm^{-1}. Solid samples were run as Nujol mulls suspended between CsI plates. The liquid samples were studied as a film of pure liquid pressed between CsI plates. The Raman spectra were obtained on the solids and neat liquids in sealed Kimex capillary tubes using a Spex Ramalog Model 1401 double-monochromator spectrometer. A CRL Model 54 Ar$^+$ laser was used for excitation. The 5145-Å line at 250-mW power was employed. Mass spectral data were obtained on a Consolidated Electrodynamics Corp. Model 21-110B spectrometer. The compounds were introduced into the source ionization chamber through either the heated oven or the direct insertion probe, depending on the sample volatility. The oven temperatures ranged from 80 to 150° and the source temperature was 75–120°. Determinations were made of the precise masses for a few of the ions but the majority of the spectra were obtained at low resolution. Because the components are relatively simple, little ambiguity arose for the assignments of the major ions from low-resolution spectra. Ion-molecule reactions corresponding to dimer and trimer formation and the addition of various radicals to the parent molecule are observed at high m/e values for all of the compounds. The ionizing energy was 70 eV.

The nuclear quadrupole resonance spectra were obtained using a Wilks Scientific NQR-IA spectrometer. Frequency measurements were made by observing the superregenerative oscillator pattern on a Tektronix 1L20 spectrum analyzer and zero-beating an external CW signal generator with the center line. The frequency of the signal generator was then measured with a Monsanto 105A electronic counter. The error in the measurements is largely a result of the uncertainty in picking the center line of the resonance multiplet and we find this to be about 0.10% in the frequency range of interest. The low-temperature spectra were obtained by inserting a dewar flask cold finger containing the sample into the radiofrequency coil.

In several instances, analytically pure samples were not obtained. The identification of the sample was secured using mass spectrometry. Since we are concerned primarily with the general spectroscopic features, four compounds not mentioned in Table I whose elemental analyses were in the range 1.2–0.5% of theoretical and whose mass spectra indicated that the compound was present in large amounts were studied further. The impurities appeared to be small amounts of chloro derivatives. It should be mentioned that a common characteristic of all of the liquid compounds prepared in this work is the very great difficulty in obtaining analytically pure samples.

Results and Discussion

Behavior of Compounds. The trivalent group Va esters and thioesters are air and moisture sensitive. Over a period of months many of the compounds decomposed giving oxides of the tri- and pentavalent states of the group Va element. In many instances the sulfides turn black upon decomposition. Only the solid samples, the arsenites, and a small number of antimonites have exhibited indefinite longevity. The arsenites and antimonites are essentially odorless, but the thio analogs are extremely offensive. One might logically expect these compounds to be extremely toxic by analogy to the corresponding phosphites. Their physical characteristics are in general accordance with previous reports[3,4] in all cases except $As(OC_6H_5)_3$, which we found to be a low-melting solid.

Vibrational Spectra. For the pyramidal EY_3 skeleton (E = As, Sb; Y = O, S) four normal modes are expected. The symmetric stretching (ν_1) and bending (ν_2) motions have A_1 symmetry. The antisymmetric stretching (ν_3) and bending (ν_4) modes have E symmetry.[5] All four modes are both Raman and ir active and in general $\nu_1 > \nu_3$ and $\nu_2 > \nu_4$ by about 15–80 cm^{-1}. The symmetric motions tend to be stronger in the Raman than in the ir while the reverse is true for the antisymmetric motions. Keeping in mind the usual limitations, we shall proceed with the assumption that the group frequencies of interest in this study are composed largely of these modes.

Y is bound to a carbon atom in the molecules so that motions due to Y-C stretching also appear. Carbon-carbon vibrations are found throughout (except for $As(OCH_3)_3$) but can be identified quite easily by comparing the ester and thio ester spectra to the parent alcohol and thiol. Since we were concerned with the $E(YC)_3$ skeleton, spectra were recorded only in the 1500–200-cm^{-1} region where its motions should lie. Tables II and III represent compilations of these skeletal assignments.

Two groups have discussed some of the details of the As-O-C vibrational motions in symmetric trivalent arsenites.[6-9] A broad band, which occasionally is resolved, occurring around 650 cm^{-1} was assigned by Shagidullin, *et al.*,[7,8] to ν_1 and ν_3. This absorption is often complex with one to four bands being present. Bands near 1000 cm^{-1} were assigned to AsO-C stretching[8] but complications can arise in these assignments because C-C modes also appear here.[10]

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Table II. Vibrational Assignments for the $E(OC)_3$ Skeleton in Arsenites and Antimonites

Compd	EO-C str	E-OC str ν_1	E-OC str ν_3	E-OC bend ν_2	E-OC bend ν_4
$As(OCH_3)_3$	995 s	617 vs[a]	575 vs	383 w	332 w[a]
$As(OC_2H_5)_3$	1094 m 1034 m	640 m[a]	610 s	391 w	356 w
$As(OC_3H_7)_3$	1056 m 1037 m	664 s[a]	625 m	377 w	336 w
$As(OC_4H_9)_3$	1071 m 1036 m	653 vs[a]	610 vs	383 w	
$As(OCH(CH_3)_2)_3$	1133 m 1115 m	682 s[a]	657 vs		328 w
$As[OC(CH_3)_3]_3$	1175 s 1030 m	665 vs[a]	632 vs	360 vs	335 vs
$As(OC_6H_5)_3$	1065 m 1019 m	680 s[a]	637 vs	370 w	
$As(OC_6H_4CH_3)_3$	1045 w 1017 w	699 s[a]	645 s	393 w	334 w
$Sb(OC_2H_5)_3$	1096 s 1045 s	587 vs[a]	540 s		325 m
$Sb(OC_3H_7)_3$	1050 s 1017 s	600 vs[a]	575 m	380 w[a]	
$Sb(OC_4H_9)_3$	1070 vs 1025 vs	610 vs[a]	570 s	360 w	337 w
$Sb[OCH(CH_3)_2]_3$	1163 m 1010 m	612 vs[a,b]	612 vs[b]		310 m
$Sb[OC(CH_3)_3]_3$	1183 s 1027 s	597 s[a]	582 s	380 w	350 w

[a] Raman frequency. [b] Sharp band in both ir and Raman.

Table III. Vibrational Assignments for the $E(SC)_3$ Skeleton in Thioarsenites and Thioantimonite Esters

Compd	ES-C str	E-SC str ν_1	E-SC str ν_3	E-SC bend ν_2	E-SC bend ν_4
$As(SC_2H_5)_3$	792 m 747 m	397 s	382 s	282 m	230 s
$As(SC_3H_7)_3$	775 s	392 vs[a]	375 vs		250 w
$As[SCH(CH_3)_2]_3$	790 s	437 s[a]	382 vs	275 m	255 w[a]
$As[SC(CH_3)_3]_3$	720 s 705 m	425 s[a]	370 vs		265 w[a]
$As(SC_6H_5)_3$	743 vs 687 vs	393 vs[a]	369 vs	296 w	
$As(SC_6H_4CH_3)_3$	720 m	400 vs[a,b]	365 m	290 m	247 m
$As(SC_6H_4Cl)_3$	739 s 692 m	400 m[a]	367 m	281 m	254 m
$Sb[SCH(CH_3)_2]_3$	700 m 610 vs	420 s[a]	373 vs		250 s
$Sb(SC_4H_9)_3$	718 m	376 s	345 s, br		
$Sb(SC_6H_5)_3$	740 s 688 s	367 s[a]	338 vs	282 w	250 s

[a] Raman mode. [b] Split into four bands.

Weak bands in the 350-450-cm^{-1} range have been assigned to the ν_2 and ν_4 bending modes.[7,8]

In the series of arsenites studied here, these assignments were found to be quite consistent. For the As-OR stretching motions strong bands appear in both the Raman and the ir spectra in the 575-699-cm^{-1} range and are assigned to ν_1 and ν_3. In several instances the expected alteration in intensity is also observed. Several weak bands in the 328-394-cm^{-1} region are assignable to the As-OR bending modes although the bands do not always appear in both the ir and Raman. Two bands in the 995-1175-cm^{-1} region are probably the symmetric and antisymmetric AsO-C motions.

Much less is known about the antimonite esters. However, bands which appear can be quite easily assigned to the skeletal modes in a fashion consistent with the arsenites. The SbO-C stretching motions are found in the 1017-1183-cm^{-1} region. ν_1 and ν_3 for Sb-OR lie at 540-612 cm^{-1}, and ν_2 and ν_4 bendings occur at 310-380 cm^{-1}.

The PO-C stretching occurs[10-14] at 1000-1080 cm^{-1}. ν_1 and ν_3 for P-OR appear[10,11,13-16] at 730-875 cm^{-1}. The trend in E-OC frequencies, which reflects mostly the mass effect, is E = P > As > Sb. Quite interestingly the EO-C motions in the 1000-1180-cm^{-1} range are not particularly sensitive to E which suggests that E-OC and EO-C stretching vibrations are not seriously coupled with one another. As the R group increases in bulk, the E-OR ν_1 and ν_3 stretching vibrations show a slight increase in frequency in most cases. A similar effect was noted in the spectra of tris(*p-tert*-butylphenyl) phosphate.[17] The bulky R groups, because of crowding, will force the pyramidal $E(OR)_3$ molecules toward planarity and this should enhance the overlap of E and O orbitals of π symmetry. It also will increase the per cent s character in the E-O σ-bonding orbitals.[18] Both effects lead to bond strengthening and thus an increase in the vibrational frequency.

The ES-R vibrational range is 624-770 cm^{-1} for E = As and Sb. The E-SR symmetric and antisymmetric stretchings lie at 365-437 cm^{-1} for E = As and 338-400 cm^{-1} for E = Sb. ν_1 and ν_3 for the analogous P-SR motions are found[19] at 500-620 cm^{-1}. As with the oxygen analogs the trend in E-SR vibrations is E = P > As > Sb. The As-SR bending motions are assigned to several bands in the 250-296-cm^{-1} region.

Mass Spectra. The hydrolysis mechanism of several arsenite esters has been studied by mass spectrometry but no fragmentation patterns were reported.[20] Data for several heterocyclic arsenic compounds RY_2AsR', where Y = O, S, have also been reported.[21]

The ions shown in Figure 1 appear in all the electron impact mass spectra. The diagram represents a reasonable fragmentation pattern for these molecules. In the majority of the esters and thio esters studied the $E(YR)_2^+$ or EYR^+ ion is most abundant. In $As(SC_3H_7)_3$ and $Sb[OC(CH_3)_3]_3$ the $E(YR)^+$ species is most abundant and in $As(OCH_3)_3$ the $OAs(OCH_3)_2^+$ ion is found to be the most abundant. This latter observation contrasts with $P(OCH_3)_3$[22] where $P(OCH_3)_2^+$ is the most abundant ion. However, as the mass of R increases, the $P(OR)_2^+$ ion decreases in importance.[22] This is not found to be the case in the arsenic and antimony homologs. Our spectrometer conditions are somewhat different from those employed previously[22] in that in the present study the probe and source temperatures were lower. This could account for the greater abundance of higher molecular weight ions found here. In a few other cases the $E(YR)_2^+$ ion is not the most abundant and these are discussed below.

A number of unusual ions not involving simple bond fission appear in high abundance in a number of the compounds.

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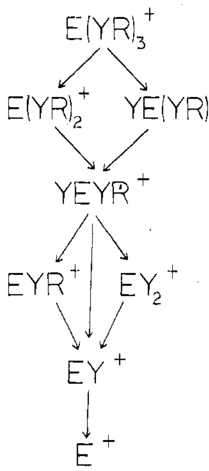
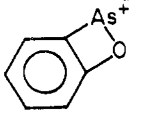


Figure 1. Possible fragmentation pattern for $E(YR)_3$ compounds (E = As, Sb; Y = O, S).

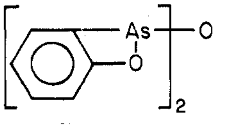
First in the alkyl arsenites, $(RCO)_nAsO^+{=}CR$ ions (n = 2, 1, 0) appear which involve rearrangement decomposition due to the loss of a single hydrogen atom. Such ions are also known in the mass spectrum of organic ethers and thioethers.[23] Similarly very abundant ions in the $Sb[OCH(CH_3)_2]_3$ and $Sb[SCH(CH_3)_2]_3$ patterns have *m/e* values corresponding to $SbOC_3H_6^+$ and $SbS_2C_6H_{13}^+$, respectively, and may involve the same structures.

The spectra of $E(YC_6H_5)_3$ compounds are particularly interesting because simple bond fissions never produced the most abundant ion. Instead, rearrangement decomposition involving the loss of one or more protons appears to take place. In $As(OC_6H_5)_3$ the ion corresponding to $As(OC_6H_4)^+$ appears. A plausible structure for this species is



The same type of ion also appears in high abundance in the mass spectra of other phenoxy and thiophenoxy derivatives, *e.g.*, $As(OC_6H_3CH_3)^+$, $As(SC_6H_3CH_3)^+$, $As(SC_6H_3Cl)^+$, $As(SC_6H_4)^+$, and $Sb(SC_6H_4)^+$.

It is interesting to note that a stable four-membered ring involving the same unit has been proposed for benzenearsenic acid anhydride.[24]



Similar ortho metalations of benzene rings are well established in transition metal chemistry[25] and also involve four-membered rings. The metal occupies the place of oxygen in these structures.

The ion $As(OC_6H_3CH_3)_2^+$ appears in the spectrum of $As(OC_6H_4CH_3)_3$. It could involve a double ortho metalation (I) or possible the biphenyl derivative (II), the analog of which has been observed in the mass spectrum of $P(C_6H_5)_3$ and $As(C_6H_5)_3$.[26]

Table IV. ^{75}As Nqr Frequencies in $As(YR)_3$ Compounds[a]

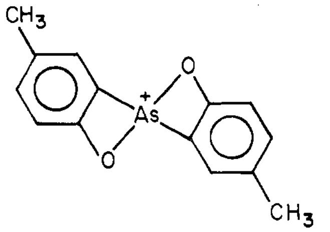
Compd	ν (^{75}As), MHz 77°K	 298°K
$As(OCH_3)_3$	113.1 (20)	
$As[OCH(CH_3)_2]_3$	109.6 (55)	
$As[OC(CH_3)_3]_3$	113.0 (5)	
$As(OC_6H_5)_3$	107.3 (5)	
$As(SC_6H_5)_3$	75.87 (3)	73.49 (30)
$As(SC_6H_4CH_3)_3$		72.04 (10)

[a] Signal-to-noise ratios are given parenthetically.

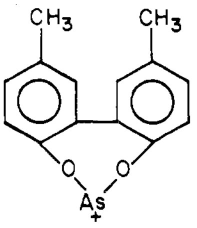
Table V. ^{121}Sb and ^{123}Sb Nqr Data in $Sb(YR)_3$ Compounds (MHz)[a]

Assignment	$Sb(SC_6H_5)_3$[b]	$Sb(OC_3H_7)_3$[c]	$Sb[OCH(CH_3)_2]_3$[c,d]
^{123}Sb $^7/_2$–$^5/_2$	108.80 (9)		
^{123}Sb $^5/_2$–$^3/_2$	68.86 (4)		101.11 (3)
^{123}Sb $^3/_2$–$^1/_2$	36.71 (15)		
^{121}Sb $^5/_2$–$^3/_2$	113.85 (40)		167.57 (7)
^{121}Sb $^3/_2$–$^1/_2$	58.28 (12)	84.79 (2)	85.80 (4)
^{121}Sb e^2Qq/h, MHz	380.9		560.6
^{121}Sb η	0.136		0.138

[a] Signal-to-noise ratios are given parenthetically. [b] 298°K. [c] 77°K. [d] From ref 30.



I



II

In the $As(OC_6H_4CH_3)_3$ pattern the most abundant ion is at *m/e* 91, probably due to $C_7H_7^+$; some contribution to this *m/e* 91 peak may come from AsO^+ however. $C_7H_7^+$ is observed in $As(SC_6H_4CH_3)_3$ for which no interferences exist and has substantial abundance there as well. $C_7H_7^+$, perhaps the tropylium ion, is a low-energy species and is prominent in the spectra of monoalkylbenzenes.[27]

Nqr Spectra. As part of a study of the electronic transmission effects in arsenic, antimony, and bismuth compounds[28,29] we recorded the ^{75}As, ^{121}Sb, and ^{123}Sb nqr spectra in the compounds. Many of the liquid samples became viscous near the freezing point and ultimately crystallized as glasses. Others appeared to pass sharply from the liquid to the solid phase but did not yield resonances. Tables IV and V list the data that were obtained. Barnes and Bray[30] reported several of the ^{121}Sb and ^{123}Sb signals in $Sb[OCH(CH_3)_2]_3$ but to our knowledge no other spectra of esters or thio esters of arsenic or antimony have been reported.

We had intended to look at the difference in transmission of the electronic character of R through O to As and Sb compared to that of S. Although the number of data points observed was small, those that were obtained are notably uninformative. The shift in the frequency of $As(OR)_3$ compounds as a function of R does not follow a recognizable trend. The dramatic decrease in the ^{75}As signals for the thio esters is consistent with an increase in the arsenic σ-bonding

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(29) T. B. Brill and G. G. Long, *Inorg. Chem.*, 11, 225 (1972).

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orbital population compared to the ester according to previous interpretations.[28] The decrease in $\nu(^{75}As)$ at 77°K compared to 298°K is normal behavior based on theory presented by Bayer.[31] The value of the electric field gradient asymmetry parameter, η, found in $Sb(SC_6H_5)_3$ suggests that the threefold axis of the molecule is retained to a reasonable degree.

Finally, in looking for ^{35}Cl signals in *p*-chlorophenyl group Va esters we found the ^{35}Cl resonances in $(p\text{-}ClC_6H_4S)_2$ at 34.07 (5), 34.28 (5), and 34.48 (5) MHz. These frequencies are almost identical with those found in meta and para chlorine atoms in substituted triphenylarsines and -stibines.[29] The ^{35}Cl signal in $NaSC_6H_4Cl$ was found at 34.55 (18) MHz for comparison.[32]

Registry No. $AsCl_3$, 7784-34-1; $SbCl_3$, 10025-91-9; C_2H_5OH, 64-17-5; C_3H_7OH, 71-23-8; $(CH_3)_2CHOH$, 67-63-0; C_4H_9OH, 71-36-3; $(CH_3)_3COH$, 75-65-0; C_6H_5OH, 108-95-2; *p*-$CH_3C_6H_4OH$, 106-44-5; C_2H_5SH, 108-98-5; C_3H_7SH, 107-03-9; $(CH_3)_2CHSH$, 75-33-2; $(CH_3)_3CSH$, 75-66-1; CH_3OH, 67-56-1; C_6H_5SNa, 930-69-8; *p*-$CH_3C_6H_4SNa$, 10486-08-5; *p*-ClC_6H_4SNa, 18803-44-6; C_4H_9SH, 109-79-5; C_6H_5SeNa, 23974-72-3; $C_6H_5SeSeC_6H_5$, 1666-13-3; $As(OCH_3)_3$, 6596-95-8; $As(OC_2H_5)_3$, 3141-12-6; $As(OC_3H_7)_3$, 15606-91-4; $As(OC_4H_9)_3$, 3141-10-4; $As[OCH(CH_3)_2]_3$, 39936-83-9; $As[OC(CH_3)_3]_3$, 23060-64-2; $As(OC_6H_5)_3$, 1529-86-8; $As(SC_2H_5)_3$, 34666-79-0; $As(SC_3H_7)_3$, 5582-57-0; $As[SCH(CH_3)_2]_3$, 39936-86-2; $As[SC(CH_3)_3]_3$, 39971-63-6; $As(SC_6H_5)_3$, 1776-70-1; $As(SC_6H_4CH_3)_3$, 39936-88-4; $Sb(OC_2H_5)_3$, 10433-06-4; $Sb(OC_3H_7)_3$, 4292-34-6; $Sb(OC_4H_9)_3$, 2155-74-0; $Sb[OCH(CH_3)_2]_3$, 18770-47-3; $Sb[OC(CH_3)_3]_3$, 10433-03-1; $Sb(SC_6H_5)_3$, 28609-58-7; $As(OC_6H_4CH_3)_3$, 1529-85-7; $As(SC_6H_4Cl)_3$, 39936-95-3; $Sb[SCH(CH_3)_2]_3$, 22141-93-1; $Sb(SC_4H_9)_3$, 22082-51-5; ^{35}Cl, 13981-72-1; ^{75}As, 7440-38-2; ^{121}Sb, 14265-72-6; ^{123}Sb, 14119-16-5.

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[32] Note Added in Proof. After acceptance of this paper, mass spectra of several arsenites and thioarsenites were reported [P. Froyen and J. Moller, *Org. Mass Spectrom.*, 7, 73 (1973)]. The assignments and fragmentation patterns are essentially in agreement with those found here.

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Mossbauer and Nuclear Quadrupole Resonance Spectra of Some Unsymmetrical Organoantimony Compounds and Nuclear Quadrupole Resonance Spectra of Some of the Arsenic Analogs

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Unsymmetrical stibines of the type $(C_6H_5)_2Sb(CH_2)_nSb(C_6H_5)_2$ show little or no asymmetry in the electric field gradient about the antimony nucleus. Large asymmetry is observed in cases where the diphenylstibino group is attached to Cl or is bound to an acetylenic linkage. This behavior is reminiscent of the occurrence of nuclear quadrupole splitting in tetravalent tin compounds and both phenomena may well arise from a common factor(s)—interaction of p electrons of the X group or polarity of the σ bonds. ^{121}Sb Mossbauer spectra of trimethylstibine and the nqr spectra of $(C_6H_5)_2AsCH_2As(C_6H_5)_2$ and *p*-$(C_6H_5)_2AsCH_2C_6H_4CH_2As(C_6H_5)_2$ have also been reported. The bond between As (or Sb) and the methylene group is electronically similar to that between As (or Sb) and the phenyl group.

Introduction

Recently, Semin, *et al.*,[1] reported nqr spectra for two symmetrical stibines, trimethylstibine and tris(*trans*-2-chlorovinyl)stibine, and for two unsymmetrical compounds, diphenylchlorostibine and bis(diphenylstibino)acetylene. The unsymmetrical compounds were found to have increased quadrupole splitting (e^2qQ/h for ^{121}Sb, ^{123}Sb respectively (MHz): 769, 980; 569.4, 726.2) as compared to the symmetrical compounds (e^2qQ/h for ^{121}Sb, ^{123}Sb (MHz): for $(CH_3)_3Sb$, 493.4, 630.6; for $(trans\text{-}ClHC{=}CH)_3Sb$, 533.0, 679.4; for $SbCl_3$, 383.6, 488.8). In addition, the unsymmetrical compounds were found to have very large asymmetry parameters ($\eta_{^{121}Sb} = \eta_{^{123}Sb}$ is 0.825 for $(C_6H_5)_2SbCl$ and 0.499 for $(C_6H_5)_2SbC{\equiv}CSb(C_6H_5)_2$). These results were ascribed to the highly asymmetric electron distribution around the Sb atom which in turn was attributed to the unsymmetrical substitution about antimony.

As part of a study of the stability of aromatic arsines and stibines as compared with the aliphatic analogs, we have determined ^{75}As or $^{121,123}Sb$ nqr spectra and ^{121}Sb Mossbauer spectra for several unsymmetrical arsines and stibines of the type $(C_6H_5)_2E\text{-}R\text{-}E(C_6H_5)_2$ (where E = As or Sb and R = CH_2, $(CH_2)_4$, $(CH_2)_{10}$, or $CH_2C_6H_4CH_2$) for comparison with spectra of symmetrical arsines and stibines, *e.g.*, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, and $(CH_3)_3Sb$. These results are reported below and it is to be particularly noted that the nqr frequencies, the quadrupole splittings, and the asymmetry parameters for these unsymmetrical stibines, in contrast to the values reported by Semin, *et al.*,[1] are very similar to those found for symmetrical stibines.[2,3]

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