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Spectra and Structure of Some Pentavalent Trimethyl - and Triphenylarsenic Derivatives

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The infrared spectra of mulls of the trimethylarsenic dihalides, $(CH_3)_3AsX_2$, are reported and assignments have been made by comparing these spectra with those of the deuterated analogs, $(CD_3)_3AsCl_2$ and $(CD_3)_3AsBr_2$. These compounds have a pentacovalent trigonal bipyramidal structure in the solid state when X is F or Cl, but have an ionic structure with tetracovalent arsenic and a halide ion when X is Br or I. ^1H and ^{19}F nmr spectra are reported for solutions of $(CH_3)_3AsF_2$ and $(CH_3)_3AsCl_2$ and are compatible with trigonal bipyramidal geometry. Triphenylarsenic difluoride, on the basis of the IR and ^{19}F nmr spectra, is a pentacovalent trigonal bipyramidal molecule, but the structures of the corresponding chloride and bromide could not be unequivocally determined from their IR spectra. The observed spectra are markedly different from spectra previously reported for these compounds by other workers. The discrepancy arises because even short exposure of triphenylarsenic dichloride or dibromide mulls to the atmosphere leads to the development of absorption peaks in the IR spectra which are characteristic of the triphenylarsenic hydroxyhalides. The IR spectra of pure samples of several trimethyl- and triphenylarsenic hydroxy compounds, R_3AsOHY, were determined and compared with the spectrum of the deuterated analog R_3AsODY.

Introduction

It has long been known that arsenic forms series of compounds having type formulas R_3AsX_2 and R_3AsOHX where R may be alkyl or aryl and X is a halogen. By analogy with the corresponding antimony compounds[1,2,3,4,5] one might anticipate that the structure of the dihalides is a trigonal bipyramid, or by analogy with the corresponding phosphorus compounds[6] that the symmetry about the arsenic is tetrahedral with one ionic halogen. Experimental evidence to date indicates that at least some of the arsenic dihalides have a trigonal bipyramidal structure.[5,7,8,9,10] Jensen,[11] however, reported that the infrared spectra of triphenylarsenic dichloride and dibromide in the solid state were significantly different from the spectra of the corresponding antimony compounds, a result which he attributed to the ionic character of the arsenic compounds. Also, kinetic studies of the reaction of triphenylarsine with iodine in chloroform solution indicated the formation of a product $[(C_6H_5)_3AsI]^+I^-$.[12,13]

Both the trialkyl and the triarylarsenic dihalides are very readily hydrolyzed to yield the so-called hydroxyhalides, R_3AsOHX.[14,15] Early investigators[14] concluded on the basis of conductivity studies that $(CH_3)_3AsBr_2$ is completely hydrolyzed in aqueous solution to $[(CH_3)_3AsOH]Br$ which behaves as a strong electrolyte. This result was confirmed and extended by Nylen.[16] Jensen,[5] on the basis of dipole moment studies of triphenylarsenic hydroxychloride in benzene solution, concluded that under these conditions, the compound exists as a resonance hybrid. $(C_6H_5)_3As^+\text{-}O^-\cdots H\text{-}Cl \leftrightarrow (C_6H_5)_3As^+\text{-}O\text{-}H\text{-}Cl^-$. Somewhat similar conclusions were reached by Hadži[17,18,19] in infrared studies of hydrogen bonding in the solid state. He considered triphenylarsine oxide as a weak base, which reacted with the strong acid, HCl, to form $[(C_6H_5)_3AsOH]^+Cl^-$, but with the weaker acid, CCl_3COOH, to form a hydrogen bonded adduct.

Results and Discussion

Trimethylarsenic dihalides. It should be possible to distinguish between the two most probable structures for the trimethylarsenic dihalides on the basis of the infrared spectra of these compounds. A pentacovalent R_3AsX_2 molecule would most likely be a trigonal bipyramid with the X groups at the apices[7] (D_{3h} point group) in which six of the eight skeletal vibrations are infrared active. If the

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compounds are salt-like, $[R_3AsX]^+X^-$, the cation should be tetrahedral (C_{3v} point group) and all six of the skeletal vibrations would be infrared active. In the pentacovalent molecule only the asymmertic carbon-arsenic stretching mode, ν_5, is infrared active, while both the symmetric, ν_1, and anti-symmetric, ν_4, are infrared active in the tetrahedral cation, $(CH_3)_3AsX^+$. Thus the two structures would be distinguishable by consideration of the carbon-arsenic stretching modes alone.

The bands between 4000 and 250 cm^{-1} in the spectrum of trimethylarsenic dichloride were assigned by comparing the spectrum of this compound with that of the deuterated analog. These assignments, along with those of the structurally similar trimethylarsenic difluoride, are listed in Table I and are typical of methylarsenic compounds.[20a,b,c] In the spectra of both trimethylarsenic dichloride and trimethylarsenic difluoride, there are only two bands above 250 cm^{-1} which were not attributable to carbon-hydrogen modes. The highest of these (662 cm^{-1} in $(CH_3)_3AsF_2$ and 642 cm^{-1} in $(CH_3)_3AsCl_2$) was assigned to the carbon-arsenic stretching mode, ν_5, which has been observed[20a] in $(CH_3)_4AsI$ at 651 cm^{-1}. The remaining band is the arsenic-halogen asymmetric stretch which occurs at 525 cm^{-1} in the fluorine compound and at 305 cm^{-1} in the chlorine compound. The absence of a carbon-arsenic symmetrical stretching mode, ν_1, indicates that the molecule belongs to the highly symmetrical D_{3h} point group in which ν_1 is infrared inactive. Accordingly, trimethylarsenic difluoride and dichloride are trigonal bipyramidal molecules in the solid state.

Only a single pmr signal was observed for $(CH_3)_3AsCl_2$ and $(CH_3)_3AsF_2$. This occurred as a singlet at 7.09τ with the dichloride and as a triplet at 7.96τ ($J_{F\text{-}H}$ = 8.6 cps) with the difluoride. A single ^{19}F nmr signal was observed in the fluorine spectrum at 53.2 ppm upfield from $CFCl_3$. These results also are consistent with trigonal bipyramidal geometry in which the halogens occupy the apical positions.

The infrared spectra of trimethylarsenic dibromide and diiodide, however, are best interpreted in terms of the structure $[(CH_3)_3AsX]^+X^-$. Again the carbon-hydrogen frequencies were identified by comparison of the spectrum of $(CH_3)_3AsBr_2$ with that of its deuterated analog $(CD_3)_3AsBr_2$, Table II. The carbon-hydrogen modes are very similar to those observed for $(CH_3)_3AsF_2$ and $(CH_3)_3AsCl_2$, except for the appearance of an

Table I. Infrared Absorption Bands of Trimethylarsenic Difluoride, Trimethylarsenic Dichloride and Trimethylarsenic Dichloride-d_9

$(CH_3)_3AsF_2$	$(CH_3)_3AsCl_2$	$(CD_3)_3AsCl_2$ **	Ratio	Assignments
2930 (w)	3010 (w) *	2255 (m)	1.33	Asym C-H st
2802 (w)	2920 (w) *	2125 (w)	1.37	Sym C-H st
1418 (m)	1408 (m)	1026 (m)	1.37	Asym C-H bend
		991 (w)		
1278 (m)	1258 (m)	977 (m)	1.29	Sym C-H bend
905 (s)				
920 (s)	935 (s) br	715 (s) br	1.31	Asym C-H rock
935 (s)				
662 (m)	642 (m)	591 (m)	1.09	Asym C-As st, ν_5
525 (s)				Asym As-F st, ν_3
	305 (s)	283 (s)	1.11	Asym As-Cl st, ν_3

s = strong, m = medium, w = weak; br = broad. * Fluorolube Mulls. ** Nujol Mull between CsBr plates.

Table II. Infrared Absorption Bands of Trimethylarsenic Diiodide, Trimethylarsenic Dibromide and Trimethylarsenic Dibromide-d_9

$(CH_3)_3AsI_2$	$(CH_3)_3AsBr_2$	$(CD_3)_3AsBr_2$	Ratio	Assignments
2990 (w) *	2991 (s) *	2550 (s)	1.33	Asym C-H st
2978 (w) *				
2890 (w) *	2900 (vw) *	2145 (vw)	1.35	Sym C-H st
		2110 (vw)		
1412 (vw) sh				
1404 (m)	1412 (m)	1028 (m)	1.37	Asym C-H bending
1395 (vw) sh	1395 (vw)	1010 (vw)	1.39	
1282 (s)	1292 (w)	989 (w)	1.31	
1265 (vw)	1278 (w)	978 (w)	1.31	Sym C-H bending
1258 (w)	1258 (w)			
948 (s)	965 (s)	748 (s)	1.29	
920 (s)	932 (s)	728 (s)	1.30	C-H rocking
855 (m)	872 (m)	670 (m)	1.30	
629 (m)	642 (m)	590 (m)	1.09	Asym C-As st, ν_4
576 (m)	582 (m)	539 (m)	1.08	Sym C-As st, ν_1
	298 (m)	293 (m)	1.01	As-Br st

s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. * Fluorolube.

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additional C-H rocking mode at 855 cm^{-1} in the diiodide and at 872 cm^{-1} in the dibromide. The carbon-arsenic asymmetric stretch, ν_4, and symmetric stretch, ν_1, are observed in the dibromide at 642 cm^{-1} and 582 cm^{-1}, respectively; in the diiodide these occur at 629 cm^{-1} and 576 cm^{-1}, respectively. The frequencies of these bands are similar to the observed asymmetric and symmetric carbon-arsenic stretching modes previously reported in the Raman spectrum of trimethylarsine (584 cm^{-1} and 572 cm^{-1}).[20b] In $(CH_3)_3AsBr_2$ a band at 298 cm^{-1}, which does not appreciably shift on deuteration, is assigned to the arsenic-bromine stretch, ν_2. This is in the same region of the spectrum where the arsenic-bromine stretching frequency has been previously reported for $(CH_3)_2AsBr$[22]. The appearance of both a symmetric and an asymmetric carbon-arsenic stretching mode in $(CH_3)_3AsBr_2$ and $(CH_3)_3AsI_2$ indicates that in the solid state these compounds are similar to $[(CH_3)_3PX]^+X^-$ rather than to the pentacovalent $(CH_3)_3AsF_2$ and $(CH_3)_3AsCl_2$. This is probably associated with the fact that bromine and iodine are considerably larger than either fluorine or chlorine, and that it might be difficult to accomodate three methyl groups and two large halogens about the arsenic.

Thus, the infrared spectra of the trimethylarsenic dihalides in the solid state are best interpreted in terms of two different structures: (a) a pentacovalent trigonal bipyramidal structure for the difluoride and the dichloride, and (b) an ionic structure $[(CH_3)_3AsX]X$ for the dibromide and the diiodide.

Triphenylarsenic dihalides. The infrared spectra of triphenylarsenic dichloride and triphenylarsenic dibromide have been previously reported to have strong bands in the 3000-2290 cm^{-1} region, a weak peak at 1200 cm^{-1} and a strong peak at 772-770 cm^{-1} which were not observed in the corresponding antimony and bismuth compounds.[11] In the present work, when the spectra of these arsenic compounds, as well as that of $(C_6H_5)_3AsF_2$, were determined under strictly anhydrous conditions, the above mentioned bands are not observed. Absorption develops at these frequencies upon exposure of the anhydrous arsenic compounds to moisture; these bands are also found to occur in the spectra of triphenylarsenic hydroxyhalides, as reported later in this paper. The spectra of these anhydrous arsenic dihalides show above 250 cm^{-1} only the frequencies expected for a monosubstituted phenyl group[21] and in the case of the fluoride, an asymmetric As-F stretching mode at 517 cm^{-1}. The so-called X-sensitive phenyl bands, listed in Table III, show an increase in frequency with an increase in mass of the halogen bonded to the arsenic. Since only the single band at 360 cm^{-1} is observed between 400 and 250 cm^{-1} in the spectrum of triphenylarsenic dichloride, the expected As-Cl frequency and an X-sensitive phenyl mode apparently are superimposed one upon the other.

Table III. X-Sensitive Vibrations

	Mode[22]			
Compound	q (a_1)	r (a_1)	y (b_1)	t (a_1)
$(C_6H_5)_3As$[21]	1082 1075	668	477 469	310
$(C_6H_5)_3AsF_2$	1088 1082	688	480	370 360
$(C_6H_5)_3AsCl_2$	1078 1068	679	468	360
$(C_6H_5)_3AsBr_2$	1070 1061	680 674	466 459	355

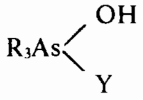
The ^{19}F nmr spectrum of triphenylarsenic difluoride shows only a single signal at 88.0 ppm upfield from $CFCl_3$ which is substantially in agreement with the results reported previously by Muetterties and coworkers.[7] On the basis of the infrared and nmr spectra, the structure of triphenylarsenic difluoride must be a pentacovalent trigonal bipyramidal molecule with two equivalent fluorines at the apices. The structures of the dichloride and the dibromide cannot be definitely assigned from our results.

The trimethylarsenic hydroxy compounds. Listed in Table IV are the infrared frequencies occurring between 4000 and 250 cm^{-1} which are associated with C-H, C-As, O-H and As-O modes in several trimethylarsenic hydroxy compounds, $(CH_3)_3AsOHY$. The assignments in Table IV are based on comparisons of the spectra of these compounds with the spectra of $(CH_3)_3AsX_2$ (Table I) and $(CH_3)_3AsODBr$ (Table IV).

The following structures need be considered for compounds of the type R_3AsOHY:

$[R_3AsY]^+OH^-$
I

$[R_3AsOH]^+Y^-$
II



III

$R_3AsO\cdots HY$
IV

Appearance of an arsenic-oxygen stretching mode would rule out structure I. Structures II and III should show an As-O absorption at a frequency above 608 cm^{-1} (the reported frequency for the symmetric As-OC mode in $(CH_3CH_2O)_3As$).[23] Due to the formation of the adduct, structure IV should show essentially an As=O stretch at a frequency which is somewhat lower than that found in trimethylarsine oxide (903 cm^{-1}).[24] The As=O frequency in triphenylarsine oxide shifts from 5 to 69 cm^{-1} when this compound acts as a donor ligand in coordination compounds; the shift was attributed to a decrease in the p_π-d_π bonding between arsenic and oxygen.[25] Indeed, we have observed a strong band near 750 cm^{-1} in all of these compounds (Table IV) which is unaffected by deuteration and which we have assigned to the arsenic-oxygen stretching frequency. We must decide, therefore, between an arsenic-oxygen single bond, at a somewhat higher frequency than that observed in $As(OCH_2CH_3)_3$ or an arsenic-oxygen double bond, shifted to a lower frequency by hydrogen bonding of an adduct. We are inclined to favor the former since the observed shifts lie between 133 and 153 cm^{-1}.

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Table IV. Infrared absorption Frequencies Associated with C-H, C-As, O-H and As-O Modes in the Spectra of Trimethylarsenic Hydroxy Compounds

$[(CH_3)_3AsOH]NO_3$	$[(CH_3)_3AsOH]ClO_4$	$[(CH_3)_3AsOH]HSO_4$	$[(CH_3)_3AsOH]Cl$	$[(CH_3)_3AsOH]Br$	$[(CH_3)_3AsOD]Br$***	Assignments
3022 (s)	3022 (s)		3010 (s)*	2995 (s)*		Asym ν (C-H)
3000 (s)			2997 (s)*			
3200-2600 (s)	3340-3180 (s)	3400-2600 (s)*	3000-2600 (s)	3060-2740 (s)	2300-2100 (s)	
2540-2300 (m)		2500-2300 (s)*	2410 (s) br	2340 (m)	1730 w) br	ν (O-H)
			1680-1610 (w)	1670-1560 (w)		
			1433 (w)*	1430 (w)*	1432 (w)	
1418 (m)* sh	1418 (m)	1413 (s)*	1423 (w)*	1420 (w)*	1420 (vw)	Asym δ (C-H)
			1410 (w)*	1405 (w)*	1408 (m)	
			1310 (w)	1305 (w)	1305 (w)	
1280 (w)			1274 (w)		1276 (w)	
1273 (m)	1278 (m)	1268 (s)	1266 (m)	1265 (s)	1268 (m)	Sym δ (C-H)
1265 (m)			1240 (w)	1240 (w)	1242 (w)	
1392 (s)*	**	**	1220 (s)	1168 (s) br	882 (m)	δ (O-H)
			942 (s)	940 (s)	942 (s)	
			931 (s)	932 (s)	935 (s)	Asym ρ (C-H)
930- 920 (s)	930 (s)	924 (s) br	926 (s)	922 (s)	926 (s)	
	917 (s) sh		918 (s)	918 (s)	918 (s)	
860 (m)	850 (m)	**	856 (m)	852 (m)	850 (m)	Sym ρ (C-H)
			847 (m)	848 (m)	830 (m)	
770 (s)	750 (s)	751 (s)	760 (s)	752 (s)	745 (s)	ν (As-O)
658 (m)	667 (m)	662 (m)	653 (m)	655 (m) sh	659 (m) sh	ν (C-As)
653 (m)	655 (m)	657 (m)		650 (m)	653 (m)	
595 (vw)			592 (w)		592 (vw)	ν (C-As)
	~580 (m) br	~595 (m) sh	692 (m)	612 (s)	445 (s)	δ (O-H)
			303 (w)			ν (As-Cl)

* Fluorolube Mull between KBr plates. ** Probably masked by broad, intense bands characteristic of the perchlorate and sulfate groups. *** Nujol Mull between KBr plates. Impurity bands from $[(CH_3)_3AsOH]Br$ are not included.

These shifts are considerably larger than those that have been found in other compounds where the $\geqslant As{=}O$ group (in triphenylarsine oxide) acts as a donor ligand.[25] This would indicate that these trimethylarsenic hydroxy compounds have essentially an As-O single bond, structures II or III.

In order to locate the frequencies associated with the As-O-H structure, the infrared spectra of trimethylarsenic hydroxybromide and its deuterated analog, $(CH_3)_3AsODBr$, were compared. Bands which shifted upon deuteration ($\nu_{OH}/\nu_{OD} \cong 1.3$) were assigned to OH stretching and bending modes (Table IV). Hydrogen bonding accounts for the complexity of the OH bands; similar behavior has been reported for compounds containing the P-O-H group.[26,27] The OH in plane bending occurs between 1392 and 1168 cm^{-1}. This mode has been observed in the case of the Sn-O-H structure at 1000 cm^{-1}.[28] The OH out of plane bending mode is observed in the trimethylarsenic hydroxy compounds near 600 cm^{-1}. This frequency is particularly strong and sharp in the halides. It is likely that structures II-IV would each exhibit hydrogen-bonding of the OH hydrogen, and, hence show complex As-O-H infrared stretching and bending modes.

The most important infrared evidence in favor of any one of the two remaining structures, II and III, should be associated with the symmetry of the Y group and the presence or absence of an As-Y stretching mode. Ideally, in compounds that correspond to the salt-like structure II, the Y group would have the symmetry of the isolated Y anion. In the tetrahedral perchlorate ion only two modes, ν_3 and ν_4, are infrared active.[29] The observed perchlorate spectrum of $[(CH_3)_3AsOH]ClO_4$ is consistent with that of an ionic perchlorate where only ν_3 (1200-1000 cm^{-1}) and ν_4 (625 cm^{-1}) are observed and the compound must have the structure shown in formula II. In trimethylarsenic hydroxynitrate the appearance of ν_2 at 1040 cm^{-1} and the spread of 130 cm^{-1} between ν_4 (1440 cm^{-1}) and ν_1 (1310 cm^{-1}) shows that the nitrate group has C_{2v} symmetry[30] and hence the structure of the compound would best be represented by structure III. However, in an acetonitrile solution of trimethylarsenic hydroxynitrate, the spectrum of the nitrate group shows only a single broad band at 1350-1300 cm^{-1} and no band at 1040 cm^{-1}; this indicates that the nitrate group now has D_{3h} symmetry. In acetonitrile solution solvation apparently stabilizes the ions $[(CH_3)_3AsOH]^+$ and NO_3^-. In the spectrum of trimethylarsenic hydroxybisulfate, bands (ν_1, 1060 (s) and 1020 (s); ν_2, 870-850 (s); ν_3, 580 (s); ν_4, 1230-1155 (s) and ν_5, 570 (s)), are present which are similar to those found for a bisulfate ion.[31]

In trimethylarsenic hydroxychloride there is a band of medium intensity at 303 cm^{-1} which can only be assigned to the As-Cl stretching mode. Except for the intensity of this band, there is little to distinguish trimethylarsenic hydroxychloride from trimethylarsenic dichloride in this region of the spectrum. The spectrum is compatible only with the pentacovalent structure for this compound. There is no absorption in the 300 to

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250 cm^{-1} region for either trimethylarsenic hydroxybromide or its deuterated analog, $(CH_3)_3As(OD)Br$. This means that the As-Br bond is ionic in these hydroxybromides or that the As-Br stretching mode occurs below 250 cm^{-1} in these compounds.

On the basis of these results we would conclude that in the solid state trimethylarsenic hydroxyperchlorate and probably trimethylarsenic hydroxybisulfate have the OH group and three methyl groups bound tetrahedrally about the arsenic and that the perchlorate and bisulfate groups occur as ions. In trimethylarsenic hydroxychloride all five groups are covalently bonded to the arsenic; the compound probably has a trigonal bipyramidal structure. The nitrate group in trimethylarsenic hydroxynitrate possesses essentially C_{2v} symmetry and the structure of the compound is probably best represented as a pentacovalent arsenic compound. The evidence for the structure of trimethylarsenic hydroxybromide is inconclusive.

Triphenylarsenic hydroxy compounds. Triphenylarsenic hydroxychloride, hydroxybromide and hydroxynitrate were synthesized. Attempts to prepare triphenylarsenic hydroxyperchlorate resulted in the formation of a compound, the analysis of which corresponded to $[(C_6H_5)_3AsO]_2HClO_4$.

The spectra of the triphenylarsenic hydroxy compounds are complicated by the presence of phenyl frequencies and broad OH bands, and it has not been found possible to assign structures to these compounds with any degree of assurance. The OH frequencies have been unambiguously assigned in the case of the hydroxybromide by preparing the deuterated analog, $(C_6H_5)_3AsODBr$ (Table V). Absorption bands, presumably associated with OH, are more complex in the hydroxychloride (2670-2450 w, 2300-2040 s, 2010-1985 m, 1630-1530 s, 1241 m and 1230 m in cm^{-1}) and in the hydroxynitrate (2400-2100 w, 1800-1600 w, 1350-1250 m, 1230-1110 m and 1030-900 m in cm^{-1}).

Table V. Infrared Absorption Frequencies Associated with the As-O-H Group in Triphenylarsenic Hydroxybromide and its Deuterated Analog

$(C_6H_5)_3AsOHBr$	$(C_6H_5)_3AsODBr$	Ratio	Assignment
2700-2580 (s)	1970-1880 (s)		
2580-2440 (s)			ν (O-H)
2330-2220 (s)	1740-1710 (s)		
1198 (m)	878 (m)	1.36	δ (O-H)
770 (s)	760 (s)	1.01	ν (As-O)

The As-O stretching mode is found at 770 cm^{-1} for triphenylarsenic hydroxybromide. However, in the other two compounds there are two or more bands between 830 and 750 cm^{-1}; any one of these could be assigned to As-O: 815, 782 and 779 cm^{-1} for the hydroxychloride and 825, 814 and 760 cm^{-1} for the hydroxynitrate (either the 825 or the 814 cm^{-1} band is due to the NO_3 group). These results clearly rule out the presence of a hydroxide ion (Structure I) at least in the case of the triphenylarsenic hydroxybromide, but are of no further assistance in arriving at the structures of these compounds.

Unfortunately, it has not been possible to make use of the symmetry of the Y group or the presence or absence of the As-Y stretching mode to help in the elucidation of the structures of these compounds. In the spectra of triphenylarsenic hydroxychloride and hydroxybromide, no arsenic-halogen stretching mode could be assigned. In the spectrum of the hydroxychloride near 300 cm^{-1} where As-Cl absorption would be anticipated, bands occur at 316 w, 303 w sh, 297 m and 289 sh cm^{-1}. However, none of these bands can be assigned to the As-Cl stretching mode since similar bands are found in triphenylarsenic hydroxybromide at 313 w, 294 m and 288 sh cm^{-1} and in triphenylarsenic hydroxynitrate at 317 w, 293 m and 288 sh cm^{-1}. This absence of As-Cl and As-Br stretching frequencies, however, cannot be taken as evidence for or against any structure, since no As-Cl or As-Br stretching modes were identified in the corresponding triphenylarsenic dihalides. In the case of triphenylarsenic hydroxynitrate, the regions where absorption for a NO_3 group would be found are complicated by the presence of broad bands, presumably associated with the OH group. The 1380-1350 cm^{-1} region, where ν_3 for the nitrate ion has been reported[30], is free of absorption. In addition, a band can be picked out at 1450 cm^{-1} which is probably ν_4 for a C_{2v} nitrate group. These observations lead us to believe that the nitrate group is covalently bound in this compound.

Experimental Section

Determination of Spectra. Infrared spectra of the compounds mulled in Nujol were determined between 4000 and 250 cm^{-1} on a Perkin-Elmer 521 infrared spectrophotometer. Since many of the compounds are very hygroscopic, the mulls were prepared and sealed between 0.004″ polyethylene sheets in a dry box. Deviations from this procedure are specifically noted.

The ^1H and ^{19}F nmr spectra were determined on a Varian HA-100 high resolution spectrometer. The pmr spectra were run on precalibrated chart paper at 500-cps sweep width with TMS as the internal «lock» reference. The ^{19}F chemical shifts were obtained by the side-band technique with $CFCl_3$ as the internal reference. The solvent in each case was $CDCl_3$.

Analysis. Elemental analyses were perfomed either by Galbraith Laboratories, Inc., Knoxville, Tennessee or Mr. R. L. Johnston of the Department of Chemistry at North Carolina State University.

Neutral equivalents were determined by the procedure suggested by Hantzsch and Hibbert[14] for trimethylarsenic dibromide. Samples were transferred in a dry box to tared, stoppered 125 ml Erlenmeyer flasks. The flasks were again weighed, the samples were dissolved in water, and titrated with standard sodium hydroxide to the phenolphthalein end point. Most of the phenyl compounds were not soluble in water and were dissolved in 95% alcohol. A correction was made for the blank.

Preparation of Compounds. Trimethylarsenic dichloride, dibromide, and *diiodide* were prepared from trimethylarsine and the appropriate halogen. The procedure of Dyke and Jones[32] was followed for prepar-

(32) W. J. C. Dyke and W. J. Jones, *J. Chem. Soc.*, 2426 (1930).

ing trimethylarsine. Formation of a perbromide or periodide was avoided by using 25% excess of $(CH_3)_3As$. Trimethylarsenic dichloride was recrystallized from absolute ethanol to give white needles, mp 156-157°.

Anal. Calcd for $C_3H_9AsCl_2$: C, 18.87; H, 4.75; neut equiv, 95.5. Found: C, 18.83; H, 4.89; neut equiv, 95.8.

Trimethylarsenic dibromide[14,16] recrystallized from acetonitrile yielded white needles, dec ~ 170°.

Anal. Calcd for $C_3H_9AsBr_2$: C, 12.88; H, 3.24; neut equiv, 140. Found: C, 13.10; H, 3.30; neut equiv, 139.

The easily decomposed trimethylarsenic diiodide was purified by dissolving the crude product in methanol at room temperature and adding ethyl ether to precipitate a light brown powder, dec ~ 130°.

Anal. Calcd for $C_3H_9AsI_2$: C, 9.64; H, 2.43; neut equiv, 187. Found: C, 9.77; H, 2.37; neut equiv, 186.

Trimethylarsenic difluoride was prepared from AgF (13.3 g as 50% water solution) and $(CH_3)_3AsCl_2$ (10.0 g in hot ethanol). After removal of the AgCl and solvent, the $(CH_3)_3AsF_2$ was distilled, bp 54° at 12 mm. The distillate (3.7 g) solidified upon standing to give a white solid mp 69-70°; yield 45%.

Anal. Calcd for $C_3H_9AsF_2$: C, 22.80; H, 5.74; F, 24.04; neut equiv, 79.0. Found: C, 22.51; H, 5.77; F, 24.24; neut equiv, 79.6.

Trimethylarsenic dichloride-d_9 and *trimethylarsenic dibromide-d_9* were prepared from methyl iodide-d_3 by the same procedures used for the nondeuterated analogs.

Anal. Calcd for $C_3D_9AsCl_2$: C, 18.02; D, 9.07. Found: C, 18.32; D, 9.60. Calcd for $C_3D_9AsBr_2$: C, 12.47; D, 6.28; Br, 55.32. Found: C, 12.56; D, 6.50; Br, 55.08.

Trimethylarsenic hydroxychloride. Trimethylarsenic dichloride (2.113 g) was neutralized with concentrated aqueous ammonia. The resulting solution was evaporated nearly to dryness and the oily residue extracted with 25 ml of acetonitrile. This $(CH_3)_3AsO$ solution was then added to an acetonitrile solution of $(CH_3)_3AsCl_2$ (2.113 g). The volume of the resulting solution was reduced to about 15 ml and upon cooling 3.1 g of $[(CH_3)_3AsOH]Cl$ was obtained. The $[(CH_3)_3AsOH]Cl$ was purified by recrystallizing from acetonitrile to give white needles, mp 133-134°.

Anal. Calcd for $C_3H_{10}AsClO$: C, 20.89; H, 5.84; neut equiv, 172. Found: C, 20.73; H, 5.96; neut equiv, 173.

Trimethylarsenic hydroxybromide. Trimethylarsenic dibromide (5.012 g) was dissolved in hot 95% ethanol. Moist ether was added to the cool solution to precipitate the solid. The crude (3.85 g) $[(CH_3)_3AsOH]Br$ was purified by recrystallization from acetonitrile, mp 149-150°.

Anal. Calcd for $C_3H_{10}AsBrO$: C, 16.61; H, 4.65; Br, 36.83; neut equiv, 217. Found: C, 16.83; H, 4.50; Br, 36.65; neut equiv, 216.

Trimethylarsenic hydroxybromide-d_1. A solution of $[(CH_3)_3AsOH]Br$ (1.5 g) in 2 ml of D_2O (99.8%) was evaporated to near dryness and the residue recrystallized from acetonitrile. The process was then repeated. Needle-like crystals of $[(CH_3)_3ASOD]Br$ (0.6 g) were obtained, mp 148-149°.

Anal. Calcd for $C_3H_9DAsOBr$: neut equiv, 218. Found: neut equiv, 218.

Trimethylarsenic hydroxyperchlorate. A solution of trimethylarsenic dichloride (1.517 g) in 30 ml of methyl alcohol was added to a solution of silver perchlorate (3.295 g) in methanol. The precipitated silver chloride was removed by filtration. Moist ether was then added until crystals of the $[(CH_3)_3AsOH]ClO_4$ (0.915 g), mp 120-121°, were obtained.

Anal. Calcd for $C_3H_{10}AsClO_5$: C, 15.24; H, 4.26. Found: C, 15.24; H, 4.55.

Trimethylarsenic hydroxybisulfate. An aqueous solution of $(CH_3)_3AsCl_2$ (7.614 g) was added to a solution of Ag_2SO_4 (12.438 g) in boiling water. The precipitated AgCl was removed by filtration and the water was removed from the filtrate at reduced pressure. An oil remained which solidified upon standing. The crude $[(CH_3)_3AsOH]HSO_4$ (9.05 g) was purified by precipitation from methanol solution with ether, mp 102-104°.

Anal. Calcd for $C_3H_{11}AsSO_5$: C, 15,39; H, 4.74; S, 13.70; neut equiv, 117. Found: C, 15.19; H, 4.88; S, 13.61; neut equiv, 117.

Trimethylarsenic hydroxynitrate. A solution of $AgNO_3$ (23.820 g) in 50 ml of water was added with stirring to an alcohol solution of $(CH_3)_3AsCl_2$ (13.390 g). The precipitated AgCl was removed and the filtrate evaporated *in vacuo* to near dryness. The crude $[(CH_3)_3AsOH]NO_3$ (12.9 g) was recrystallized from 3-pentanone to yield needle-like crystals, mp 129-130° (Lit. 127°).[33]

Anal. Calcd for $C_3H_{10}AsNO_4$: C, 18.10; H, 5.06; N, 7.04; neut equiv, 199. Found: C, 18.05; H, 5.04; N, 6.90; neut equiv, 198.

Triphenylarsenic dichloride and *dibromide* were prepared according to published methods.[15]

Anal. Calcd for $C_{18}H_{15}AsCl_2$: C, 57,32; H, 4.01; neut equiv, 189. Found: C, 57.24; H, 4.15; neut equiv, 190. Calcd for $C_{18}H_{15}AsBr_2$: C, 46.39; H, 3.24; Br, 34.29; neut equiv, 233. Found: C, 46.46; H, 3.30; Br, 34.09; neut equiv, 233.

Triphenylarsenic difluoride was prepared from $(C_6H_5)_3AsCl_2$ (8.00 g) in 225 ml of ethanol and AgF (5.39 g) in 10 ml water. The silver chloride was removed by filtration and the filtrate was concentrated by boiling to a volume of 100 ml. Upon cooling, crystals of $(C_6H_5)_3AsF_2$ (5.40 g) formed. The $(C_6H_5)_3AsF_2$ was recrystallized from absolute ethanol to yield needle-like crystals, mp 139-140°. (Lit. 135-137°).[34]

Anal. Calcd for $C_{18}H_{15}AsF_2$: C, 62.81; H, 4.39; neut equiv, 172. Found: C. 62.53; H, 4.37; neut equiv, 173.

Triphenylarsenic hydroxychloride[15] and *hydroxybromide* were obtained by hydrolysis of the corresponding dihalides in aqueous alcohol. The compounds were recrystallized from a benzene-alcohol mixture.

Anal. Calcd for $C_{18}H_{16}AsClO$: C, 60.27; H, 4.50; neut equiv, 359. Found: C, 60.69; H, 4.49; neut equiv, 359. Calcd for $C_{18}H_{16}AsBrO$: C, 53.63; H, 4.00; neut equiv, 403. Found: C, 53.82; H, 3.93; neut equiv, 405.

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(33) G. A. Razuvaev, V. S. Malinovskii and D. A. Godina, *Zh. Obshch. Khim.*, Ser. A 5, 721 (1935).

(34) W. C. Smith, *J. Am. Chem. Soc.*, 82, 6176 (1960).

Triphenylarsenic hydroxynitrate. Triphenylarsenic dichloride (3.000 g) in 50 ml of alcohol was treated with a solution of silver nitrate (2.700 g) in 50 ml aqueous ethyl alcohol. After removal of the precipitated silver chloride the filtrate was evaporated on the hot plate to yield a yellow oil which solidified on standing. Recrystallization from benzene yielded 2.50 g of the purified $(C_6H_5)_3AsO.HNO_3$.

Anal. Calcd for $C_{18}H_{16}AsNO_4$: C, 56.12; H, 4.19; N, 3.64. Found: C, 56.86; H, 4.26; N, 3.65.

Attempted preparation of Triphenlarsenic Hydroxyperchlorate. Triphenylarsenic dichloride (2.406 g) dissolved in 50 ml ethyl alcohol was added to a solution of silver perchlorate (2.630 g) in 50 ml ethyl alcohol. The precipitated AgCl was removed by filtration. About 400 ml of water was added to the filtrate and white crystals (1.715 g), mp 210-211°, were obtained. Analysis of the product indicated that it could be formulated as $[(C_6H_5)_3AsO]_2HClO_4$.

Anal. Calcd for $C_{36}H_{31}As_2ClO_6$: C, 58.04; H, 4.19; neut equiv, 745. Found: C, 57.40; H, 4.25; neut equiv, 748.

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