Vibrational Spectroscopic Study of Trimethylarsine–Boron Trihalide Adducts

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The vibrational spectra of $AsR_3{\cdot}{}^{10}BX_3$ (R = CH_3 or CD_3; X = Cl or Br) and $AsR_3{\cdot}{}^{n}BX_3$ (R = CH_3 or CD_3; X = Cl, Br, or I; n = natural abundance) are reported. The BAs stretching frequencies are assigned between 640 and 740 cm^{-1}, and the calculated force constants (2.84, 2.26, and 1.70 mdyn Å^{-1}) show that the BAs bond strength decreases for the adducts in the sequence BI_3 > BBr_3 > BCl_3. The order of BAs bond strength is the same as that of the adduct stabilities as determined by calorimetry.

It is known that trialkylarsines react with diborane to form 1 : 1 addition compounds similar to those of the corresponding phosphorus and nitrogen compounds, although those involving BAs bonding are less stable.[1,2] The normal-co-ordinate analysis (n.c.a.) carried out recently on $AsMe_3{\cdot}BH_3$ [3,4] allowed, for the first time, a comparison of the BAs bond strengths (in terms of force constants) with BN and BP bond strengths of similar compounds. However, no boron–ligand stretching force constants for other BAs compounds are known.

In recent work by Denniston and Martin [5] and also by Mills and co-workers,[6,7] the preparation and properties of $AsMe_3{\cdot}BX_3$ were reported. The i.r. and Raman spectra presented [7] are however incomplete and the assigned BAs stretching frequency between 181 and 221 cm^{-1} appeared to be quite low.

In this work we present, in more detail, the vibrational spectra and the n.c.a. of $AsMe_3{\cdot}BX_3$ (X = Cl, Br, or I). Of particular interest is a comparison of the bond strengths in our adducts with those in $AsMe_3{\cdot}BH_3$, and of the calculated BAs stretching force constants with the adduct stabilities determined by calorimetry.[6,7]

EXPERIMENTAL

Materials.—The compounds AsR_3 (R = CH_3 or CD_3) were prepared using the previously described method.[4] Boron-10 trichloride and tribromide were prepared by the reaction of freshly sublimed or distilled $AlCl_3$ or $AlBr_3$ with dried $K[{}^{10}BF_4]$ (95% enriched in ^{10}B) in a sealed glass ampoule provided with a break-seal, at 423—443 K during 4—6 h.[8] The final products were purified by trap-to-trap distillation and stored in a break-seal ampoule. Similarly, natural-abundance BCl_3 and BBr_3 were always purified before use. High-purity BI_3 (only in natural abundance) was used without further purification.

Preparation of the Adducts.—All the preparations were carried out in a high-vacuum line. The adducts of BCl_3 and BBr_3 were prepared by condensing trimethylarsine and the boron trihalide in a 1 : 1 mol ratio in a glass tube (*ca.* 1 cm^3) cooled to 77 K. The tube was immersed in a bath at *ca.* 189 K for the BCl_3 compounds and *ca.* 228 K for the BBr_3 compounds. The products were dried at room temperature by opening the system to the vacuum line. The adduct $AsMe_3{\cdot}BI_3$ was prepared by dissolving first a known amount of BI_3 crystals in benzene. The tube containing this solution was then cooled to 77 K and a slight excess of trimethylarsine was condensed into it. The reaction was completed by gradually warming the reaction tube to room temperature. The product was dried under vacuum during 30 min and stored under vacuum, protected against light.

Spectroscopic Measurements.—Infrared spectra of the solids were recorded between 400 and 4 000 cm^{-1} by subliming the sample onto a CsI window cooled to 77 K. The solid film was annealed at room temperature for 30 min for the BCl_3 and BBr_3 compounds and nearly 60 min for the BI_3 compound. All the spectra were recorded at 77 K. Far-i.r. spectra between 33 and 400 cm^{-1} were obtained at room temperature with the samples as Nujol mulls. Raman spectra of the solids in a glass capillary tube were recorded at room temperature. The low solubility of these compounds in all common solvents [7] hindered polarization measurements. Only a poor spectrum was obtained for the BCl_3 compound in CH_2Cl_2. The equipment used and the calibration procedure were as described previously.[4]

RESULTS

Assignments.—For all the adducts the assignments were made for C_{3v} molecular symmetry for which the 10 A_1 and 15 E modes are both i.r. and Raman active while 5 A_2 is inactive in both spectra. The designation of the fundamentals is given in Table 1. The vibrational frequencies are given in Tables 2—6. The assignment of the fundamental frequencies of the Me_3As moiety was straightforward by comparison with the assignments of the free ligand,[9,10] trimethylarsine–borane,[3,4] and other complexes of trimethylarsine.[11,12]

TABLE 1

Approximate description and numbering of the fundamental vibrations of $AsMe_3{\cdot}BX_3$

A_1	A_2	E	
ν_1	ν_{11}	ν_{16}, ν_{17}	CH_3, CD_3 asym str.
ν_2		ν_{18}	CH_3, CD_3 sym str.
ν_3	ν_{12}	ν_{19}, ν_{20}	CH_3, CD_3 asym def.
ν_4		ν_{21}	CH_3, CD_3 sym def.
ν_5	ν_{13}	ν_{22}, ν_{23}	CH_3, CD_3 rock.
ν_6			BAs str.
ν_7		ν_{25}	AsC_3 str.
ν_8		ν_{24}	BX_3 str.
ν_9		ν_{27}	AsC_3 def.
ν_{10}		ν_{26}	BX_3 def.
		ν_{28}	AsC_3 rock.
		ν_{29}	BX_3 rock.
	ν_{14}	ν_{30}	CH_3, CD_3 torsion
	ν_{15}		BX_3 torsion

$AsMe_3{\cdot}BCl_3$, 100—800 *cm*$^{-1}$.—In this region the i.r. spectrum is characterized by a strong band near 735 cm^{-1} for ^{10}B and near 705 cm^{-1} for ^{11}B compounds. These are associated with the BCl_3 degenerate stretching (ν_{24}) and are in reasonable agreement with the expected ^{10}B–^{11}B isotopic shift. The corresponding symmetric stretching (ν_8) is assigned to the band near 370 cm^{-1} which was confirmed by polarization measurement. The band near 255 cm^{-1} is easily assigned to the BCl_3 degenerate deformation (ν_{26}), while the assignment of the corresponding symmetric deformation (ν_{10}) is difficult because it varies according to the ligand.[13-16] The bands between 160 and 175 cm^{-1} observed with strong to medium intensities in both spectra were assigned as ν_{10}. The position of this band is almost the same as that observed for $PMe_3{\cdot}BCl_3$,[16] *i.e.* 160 cm^{-1}, but considerably lower in relation to $NMe_3{\cdot}BCl_3$,[15] *i.e.* 270 cm^{-1}.

TABLE 2

Infrared bands (cm^{-1}) of $AsMe_3{\cdot}BCl_3$ at 77 K

^{10}BH [a]	^{10}BD	^{11}BH [b]	^{11}BD	Assignment
3 917vw		3 910vw		$\nu_1 + \nu_5$
3 840vw		3 830vw		$\nu_2 + \nu_5$
3 010m	2 250m	3 011m	2 253m	$\nu_1, \nu_{16}, \nu_{17}$
2 923m	2 123m	2 919m	2 128m	ν_2, ν_{18}
1 902vw		1 900vw		$\nu_4 + \nu_{25}$
1 857vw		1 850vw		$\nu_4 + \nu_7$
1 403s	1 031m	1 400s	1 033m	ν_{19}
1 390m	1 029	1 387	1 030w(sh)	ν_3, ν_{20}
1 288w		1 287w		?
1 272m	988m	1 273m	988m	ν_{21}
1 265m	986m	1 266m	984m	ν_4
926		925		
919 s	696s	919 s	692(sh)	ν_{22}
911	689(sh)	912	681s	ν_5
834w	636s	835w	633s	ν_{23}
735vs,br	736vs	737m	742m	ν_6, ν_{24}
708m		705vs	717vs	
702w			704vs	
640m	584w	641m	584w	ν_{25}
594s	540m	593s	538m	ν_7
373m	371w	374m	370w	ν_8
259m	255m	259m	255m	ν_{26}
230m	212m	231m	214m	ν_9, ν_{27}
	185w		186w	ν_{28}
174m	163m	174m	165m	ν_{10}
		131vw		ν_{29}

[a] v = Very, w = weak, s = strong, m = medium, br = broad, sh = shoulder. Abbreviations of compounds: ^{10}BH, $AsMe_3{\cdot}{}^{10}BCl_3$; ^{10}BD, $As(CD_3)_3{\cdot}{}^{10}BCl_3$; ^{11}BH, $AsMe_3{\cdot}{}^{11}BCl_3$; and ^{11}BD, $As(CD_3)_3{\cdot}{}^{11}BCl_3$. [b] Boron-11 represents the normal isotopic distribution.

TABLE 3

Raman bands (cm^{-1}) of $AsMe_3{\cdot}BCl_3$ at room temperature

^{10}BH [a]	^{10}BD	^{11}BH	^{11}BD	^{10}BD [b]	Assignment
3 015vw	2 260m	3 010vw	2 259m	2 259m	$\nu_1, \nu_{16}, \nu_{17}$
2 929w	2 133m	2 926w	2 132m	2 133m,p	ν_2, ν_{18}
1 411vw	1 029m	1 411vw	1 030m	1 030vw	ν_3, ν_{20}
1 283vw		1 288w			?
1 265vw	990m	1 270w	991m	991m,p	ν_4
915(?)	681m	920(?)	675m		ν_5
843vw	640w	846w	635w		ν_{23}
738w	735w	732vw	743vw		ν_6, ν_{24}
		700m	720w		
640s	585s	640s	586s	582m	ν_{25}
592vs	543vs	591vs	543vs	541s,p	ν_7
373s	371vs	373vs	372s	372s,p	ν_8
256s	253s	258s	255s		ν_{26}
226m	211vw	231m	212w	211vw	ν_9, ν_{27}
208s	187m	211s	185m		ν_{28}
170vs	160vs	175vs	163vs	165m,p(?)	ν_{10}
130vw					ν_{29}?

[a] See footnote *a* to Table 2. [b] Spectrum in CH_2Cl_2, p = polarized.

By comparison with $AsMe_3{\cdot}BH_3$, the BAs stretching mode (ν_6) should be expected between 450 and 510 cm^{-1}, but no band in this region was observed for the BCl_3 compound. However, the trend of boron–ligand stretching frequency in $NMe_3{\cdot}BCl_3$ and $PMe_3{\cdot}BCl_3$ complexes [13-16] suggests that the BAs mode is accidentally degenerate with ν_{24} in our case. This assignment is clearly supported by the spectrum of the BBr_3 and BI_3 compounds, where ν_6 is relatively well separated from ν_{24}.

$AsMe_3{\cdot}BBr_3$, 90—800 *cm*$^{-1}$.—The i.r. spectra show a strong absorption near 715 and 670 cm^{-1} for the ^{10}B and ^{11}B complexes. These bands, which appear with medium intensity in the Raman spectra, were assigned to ν_6. The strong i.r. bands, well separated from ν_6, at 651 and 663 cm^{-1} for ^{10}BH and ^{10}BD compounds, were assigned to ν_{24}. For the natural-abundance ^{11}BH and ^{11}BD compounds, although the i.r. spectrum is very complex in this region, ν_{24} was assigned at 616 and 608 cm^{-1}. The band near 240 cm^{-1}, which is strong in the Raman and medium in the i.r. spectrum, was assigned to ν_8. The deformation modes, ν_{10} at *ca.* 130 cm^{-1} and ν_{26} at *ca.* 145 cm^{-1}, were assigned by comparison with those made for $PMe_3{\cdot}BBr_3$.[16] Again ν_{10} is considerably lower compared with $NMe_3{\cdot}BBr_3$ [15] (*ca.* 196 cm^{-1}). The ν_{29} vibration was not assigned although a weak band was observed at *ca.* 90 cm^{-1} in both spectra.

$AsMe_3{\cdot}BI_3$, 70—700 *cm*$^{-1}$.—The band near 650 cm^{-1}, which appears with medium to strong intensity in both spectra, is reliably assigned to ν_6. The band near 543 cm^{-1} is assigned to ν_{24}, taking into account the i.r. intensity and the expected lower value for this mode in BI_3, than in BCl_3.

The only reasonable assignments for ν_8 are the bands which appear very strongly in the Raman at 167 and 162 cm^{-1} for ^{11}BH and ^{11}BD respectively, assuming that this mode is accidentally degenerate with ν_{28}. For the remaining frequencies, by comparison with the assignments made for $PMe_3{\cdot}BI_3$ [16] and $PI_3{\cdot}BI_3$,[17] those at *ca.* 110, 97, and 71 cm^{-1} were assigned to ν_{10}, ν_{26}, and ν_{29}, respectively.

The product-rule ratios compared with the theoretical ratios of the determinant of the *G* matrices (in parentheses), calculated for A_1 symmetry only, are: ^{10}BH : ^{10}BD = 5.42 (5.53), ^{10}BH : ^{11}BH = 1.00 (1.05), ^{10}BH : ^{11}BD = 5.51 (5.78) for $AsMe_3{\cdot}BCl_3$; ^{10}BH : ^{10}BD = 5.21 (5.57), ^{10}BH : ^{11}BH = 1.05 (1.05), ^{10}BH : ^{11}BD = 5.74 (5.83) for $AsMe_3{\cdot}BBr_3$; and ^{11}BH : ^{11}BD = 5.48 : 1 (5.59 : 1) for $AsMe_3{\cdot}BI_3$.

These results give some support for the assignments. (For the abbreviations ^{10}BH, ^{10}BD, *etc.* see the footnote in Table 2.)

Normal-co-ordinate Analysis.—The structural parameters were taken from $AsMe_3{\cdot}BH_3$ [3] and $NMe_3{\cdot}BX_3$: [18] r(BAs) = 2.035, r(AsC) = 1.945, r(CH) = 1.090, r(BCl) = 1.83, r(BBr) = 2.04, and r(BI) = 2.28 Å (1 Å = 100 pm); CAsC 105°. The geometry around C and B atoms was assumed to be tetrahedral. The symmetry co-ordinates were similar to those described elsewhere.[4] In the calculations the frequencies were weighted by $1/\lambda$ and the initial set of force constants transferred from $AsMe_3{\cdot}BH_3$ [4] and $MeCN{\cdot}BX_3$.[19] The least-squares refinement was carried out in terms of symmetry force constants, which were fitted to the observed frequencies of all isotopes simultaneously.

TABLE 4

Infrared bands (cm^{-1}) of $AsMe_3{\cdot}BBr_3$ at 77 K

^{10}BH *	^{10}BD	^{11}BH	^{11}BD	Assignment
3 898vw		3 900vw		$\nu_1 + \nu_5$
3 821vw		3 820vw		$\nu_2 + \nu_5$
2 995m	2 251m	2 995m	2 250m	$\nu_1, \nu_{16}, \nu_{17}$
2 912m	2 125m	2 915m	2 126m	ν_2, ν_{18}
		1 900vw	1 561vw	$\nu_4 + \nu_{25}$
		1 845vw	1 516vw	$\nu_4 + \nu_7$
1 399s	1 030s	1 396s	1 030s	ν_{19}
1 390w	1 027(sh)	1 387m	1 027(sh)	ν_3, ν_{20}
1 286w		1 286w		?
1 267(sh)	987m	1 270m	988m	ν_{21}
1 264m	983m	1 264m	984m	ν_4
922 918 } s		923 918 } s		ν_{22}
912m	690s	910m	688m	ν_5
835w	620vs	834m	622m	ν_{23}
715s	715s	715m	716m	ν_6 (^{10}B)
683vw		687s	669vs	ν_6 (^{11}B)
651vs	663vs	651s	651s	ν_{24} (^{10}B)
620w	607w	616vs	608vs	ν_{24} (^{11}B)
636s	581w	640vs	582m	ν_{25}
590m	538m	588s	538m	ν_7
246m	240m	247m	240m	ν_8
	190w	213w	189w	ν_9, ν_{27}
185m	175w	184m	173w	ν_{28}
147m	143w	147m	143m	ν_{26}
	130vw	128vw	125w	ν_{10}
	94w		93w	ν_{29}?

* See footnote *a* to Table 2.

TABLE 5

Raman bands (cm^{-1}) of $AsMe_3{\cdot}BBr_3$ at room temperature

^{10}BH *	^{10}BD	^{11}BH	^{11}BD	Assignment
3 010w	2 258w	3 010w	2 257w	$\nu_1, \nu_{16}, \nu_{17}$
2 924m	2 129m	2 924m	2 129m	ν_2, ν_{18}
1 408m	1 027w	1 408m	1 028m	ν_{19}
1 286vw		1 285w		?
1 265vw	989m	1 264w	988m	ν_4
919vw	679m	919(?)		ν_{22}
843w	630w	843w		ν_{23}
708m	720w	709vw		ν_6 (^{10}B)
		678m	671m	ν_6 (^{11}B)
	665(sh)			ν_{24} (^{10}B)
		619m	610vw	ν_{24} (^{11}B)
633vs	584vs	637m	582vs	ν_{25}
589vs	541m	587vs	540vs	ν_7
243vs	242vs	246vs	241vs	ν_8
210vs	196vs	214vs	192vs	ν_9, ν_{27}
179s	172s	184m	170s	ν_{28}
143(sh)	140s	146m	143s	ν_{26}
130w	133s	134s	130s	ν_{10}
	84vw		85m	ν_{29}?

* See footnote *a* to Table 2.

Since it was not possible to refine all the significant off-diagonal symmetry force constants, the best estimated values, determined from various trial refinements, were constrained in the last least-squares cycle. Due to the uncertainty of assignment for the BX_3 rocking in BCl_3 and BBr_3 adducts, the corresponding force constant, $F_{29,29}$, was directly transferred from $MeCN{\cdot}BX_3$ [19] and constrained. The torsional mode was not included in the calculations.

Infrared frequencies were used to compute the force constants, while below 400 cm^{-1} Raman frequencies were used because the far-i.r. spectrum was very noisy and the bands were relatively broad.

The calculated symmetry force constants and calculated frequencies are presented in Supplementary Publication No. SUP 22799 (6 pp.).*

TABLE 6

Infrared bands (cm^{-1}) at 77 K and Raman bands (cm^{-1}) at room temperature of $AsMe_3{\cdot}{}^{11}BI_3$

Infrared		Raman		
^{11}BH *	^{11}BD	^{11}BH	^{11}BD	Assignment
3 900vvw				$\nu_1 + \nu_5$
3 824vvw				$\nu_2 + \nu_5$
2 994m	2 244m	2 995w	2 244m	$\nu_1, \nu_{16}, \nu_{17}$
2 914m	2 112m	2 910s	2 117s	ν_2, ν_{18}
	1 560vw			$\nu_4 + \nu_{25}$
	1 510vw			$\nu_4 + \nu_7$
1 411m	1 028m	1 400m	1 020m	ν_{19}
1 397s	1 023s			ν_3, ν_{20}
1 281w				?
1 270m	984w	1 274m		ν_{21}
1 257m	978m		978s	ν_4
	776vw			?
917(sh)	724vs			ν_{22}
907vs	707vs	907w	702w	ν_5
829vw		824w	610w	ν_{23}
685w	668m	675w	662vw	ν_6 (^{10}B)
658m	646s	648s	636s	ν_6 (^{11}B)
632s	580vs	629vs	576vs	ν_{25}
577s	530ms	575vs	530vs	ν_7
573(sh)	563ms		560w	ν_{24} (^{10}B)
546vs	540vs	544s		ν_{24} (^{11}B)
229m	205m	223s	199s	ν_9
210(?)	186vw	214s	183s	ν_{27}
172m	166w	167vvs	162vvs	ν_8, ν_{28}
	158m			?
116m	113m	110m	107m	ν_{10}
99m	95m	99m	95m	ν_{26}
72m	70m	72m	70m	ν_{29}

* See footnote *a* to Table 2.

DISCUSSION

The modes in the trimethylarsine part of the adduct which show a large shift are the AsC_3 symmetric and asymmetric stretching. The calculated force constants indicate that the AsC bond is strengthened in the complexes, *i.e.* average f(AsC) = 2.93 mdyn Å^{-1}, in comparison with free trimethylarsine where f(AsC) = 2.56 mdyn Å^{-1} (Table 7).† This bond strengthening may result, as rationalized for $AsMe_3{\cdot}BH_3$, from a rehybridization around the As atom to give a higher s character in the AsC bond.[3] Little significance may be attached to the variation in f(AsC) from Cl to I since the constraints used for $F[\rho(CH_3,CD_3),\nu(AsC_3)]$ of E species slightly affect

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

† Throughout this paper: 1 dyn = 10^{-5} N.

TABLE 7

Symmetry force constants (f/mdyn Å^{-1}) and thermodynamic data (ΔH/kJ mol^{-1})

	$AsMe_3{\cdot}BX_3$			$AsMe_3$ [a]	$AsMe_3{\cdot}BH_3$ [b]	BX_3 [c]		
	Cl	Br	I			Cl	Br	I
f(BAs)	1.70	2.26	2.84		1.85			
f(BX) + 2f(BX, BX)	2.95	2.51	1.94			4.89	3.75	2.70
f(BX) − f(BX, BX)	2.57	1.75	1.48			2.49	2.55	1.47
f(AsC) + 2f(AsC, AsC)	2.89	2.90	2.86	2.56	2.92			
f(AsC) − f(AsC, AsC)	3.09	2.98	2.82	2.56	3.17			
$-\Delta H_r$ [d]	193	340			207			

[a] Ref. 3. [b] Ref. 4. [c] The force constants are those of ref. 20(*a*); however, see also refs. 20(*b*)—(*d*), since the values of f(BX) − f(BX, BX) of the three BX_3 compounds are very discrepant. [d] For the reaction: acid(g) + base(g) ⟶ adduct(s).[6]

the value of this force constant. Comparing the BX stretching force constants of the adducts with those of free BX_3,[20] the usual decrease for the adducts is observed. The largest changes are found for lighter acids where the decrease in strength of the BX π bond should be larger upon formation of the donor–acceptor bond.[19]

In the previous work of Mente and Mills,[7] the BAs stretching force constants calculated *via* a diatomic oscillator model are very approximate. The potential-energy distribution showed that ν_6 is very highly coupled and basically this mode originates from BAs stretch mixed with BX_3 (sym) stretch and BX_3 (sym) deformation. It was also observed that the contribution of BAs stretch changes for each adduct, as a consequence of which the frequency ν_6 decreases from Cl to I.

The increase of BAs stretching force constants along the series $BCl_3 < BH_3 < BBr_3 < BI_3$ in $AsMe_3{\cdot}BX_3$ and $AsMe_3{\cdot}BH_3$ follows the sequence of adduct stability determined by calorimetry,[6] except for BI_3 for which the enthalpy of reaction is not known.

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