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Vibrational Spectra and Normal Coordinate Calculations for Trimethylarsine–Borane

Fumio WATARI

Department of Applied Science, Faculty of Engineering, Tohoku University, Sendai 980

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Studies were carried out on the infrared spectra (33—4000 cm^{-1}) of eight isotopic trimethylarsine–boranes, $(CH_3)_3AsBH_3$, $(CH_3)_3As^{10}BH_3$, $(CH_3)_3AsBD_3$, $(CH_3)_3As^{10}BD_3$, $(CD_3)_3AsBH_3$, $(CD_3)_3As^{10}BH_3$, $(CD_3)_3AsBD_3$, and $(CD_3)_3As^{10}BD_3$, in the solid state at low temperature, and on the Raman spectra (0—4000 cm^{-1}) in the solid state and in solution of dichloromethane at room temperature. The spectra were interpreted on the basis of C_{3v} molecular symmetry, complete assignments for all fundamentals except the internal torsion being made. Normal coordinate calculations were carried out utilizing a symmetry force field in order to confirm the assignments. One of the methyl rocks was found to be mixed with the borane rock, making the assignments of these frequencies complicated. The As–B and As–C force constants were found to have the values 1.849 and 3.087 mdyn/Å, respectively.

Group IIIb and Group Vb compounds form the so-called Lewis acid–base complexes. Reactions of diborane with several trialkyls of Group Vb elements and properties of the complexes were discussed by Hewitt and Holiday.[1] As regards phosphorus–boron and arsenic–boron bonding, Burg and Wagner,[2] and Stone and Burg[3] reported the preparation and properties of several phosphine–boranes and arsine–boranes. The arsine-borane compounds are less stable than the corresponding phosphine–boranes. Trimethylarsine–borane is slightly sensitive to water vapor, but stable at room temperature when kept in a vacuum or an inert gas atmosphere.

In studing these electron donor-acceptor complexes, the properties of the donor-acceptor bonds are of interest. Durig *et al.*[4] reported on microwave, vibrational, and NMR studies. During a course of vibrational studies on trimethylarsine oxide[5] and other trimethylarsine addition compounds, vibrational assignments obtained for trimethylarsine moiety were found to differ from the assignments of Durig *et al.* A detailed vibrational study was considered necessary for consistent assignments. A report is given herewith on infrared and Raman studies of trimethylarsine–borane for eight isotopic compounds prepared from $(CH_3)_3As$, $(CD_3)_3As$, B_2H_6, B_2D_6, $^{10}B_2H_6$, and $^{10}B_2D_6$ (the relative abundances of two isotopes in natural boron are 80.4% ^{11}B and 19.6% ^{10}B). The vibrational assignments were made by means of normal coordinate calculations.

Experimental

All the preparative work was carried out in a conventional vacuum-line. Spectral measurements were made in a vacuum. Trimethylarsine-d_0 and -d_9 were prepared by reactions of Grignard reagents, CH_3MgI and CD_3MgBr, with $AsCl_3$. B_2H_6 was prepared by the addition of BF_3–ether complex to $LiAlH_4$ suspension in ether.[6] B_2D_6 was prepared in a similar manner using $LiAlD_4$. In the preparation of ^{10}B isotopic diboranes, $^{10}BF_3$–ether complex was used, which was obtained by dissolving $^{10}BF_3$ gas in ether evolved by the thermal decomposition of $K^{10}BF_4$ at 750 °C.[7]

Trimethylarsine-borane complex was prepared by condensing trimethylarsine and diborane in a 2 : 1 mole ratio into a small reaction tube fitted with a stopcock at liquid nitrogen temperature. After closing the stopcock the tube was left to stand until it attained room temperature. It was then immersed in a -22 °C bath (carbon tetrachloride slush) and opened to the vacuum-line to remove volatile substances.

Infrared spectra were recorded on a Perkin-Elmer Model 337 in the region 400—4000 cm^{-1}. Frequencies were read on a Hitachi QPD-33 recorder by abscissa expansion with use of a Perkin-Elmer Expanded Scale Readout Kit. The instrument was calibrated in the ususal manner.[8] The spectra were obtained for the samples deposited onto a CsI plate cooled by liquid nitrogen. Before recording the spectra, the samples were annealed till there was a slight increase in intensity of absorption over that immediately after deposition.

Far infrared spectra were obtained between 33 and 400 cm^{-1} with a Hitachi FIS-III spectrophotometer which was evacuated in order to remove atmospheric water vapor. The instrument was calibrated with water vapor frequencies. The sample was sublimed onto a polyethylene window which was cooled by liquid nitrogen. The sample was annealed in a similar way to that for the mid-infrared study. The double chopping method was used to avoid the radiation effect resulting from the temperature difference between the sample and reference beam paths.

Raman spectra were recorded from 0 to 4000 cm^{-1} on a JEOL JRS-Sl laser Raman spectrophotometer equipped with a NEC GLG 108 He-Ne laser. The Raman spectrophotometer was calibrated with the emission lines of neon. The spectra were obtained at room temperature in the solid state and in CH_2Cl_2 solutions sealed into capillaries of about 1.5 mm o.d.

Results and Vibrational Assignments

The infrared spectra of ^{10}B complexes are shown in Fig. 1, and the Raman spectra of solid ^{10}B compounds in Fig. 2. In the far infrared spectra, only two absorptions were observed, one very weak and the other intense but broad. Since these frequencies are not sufficiently accurate because of high noise level and broadness, the spectra are not shown and no frequency data are used in this study.

If we assume a molecular symmetry of C_{3v}, we see from group theory that its 45 molecular vibrations are distributed as $10A_1+5A_2+15E$, in which A_1 and E vibrations are active in both infrared and Raman spectra, A_2 being inactive in both.

Nearly all the vibrations are observed in the region expected from trimethylarsine,[9] trimethylarsine addi-

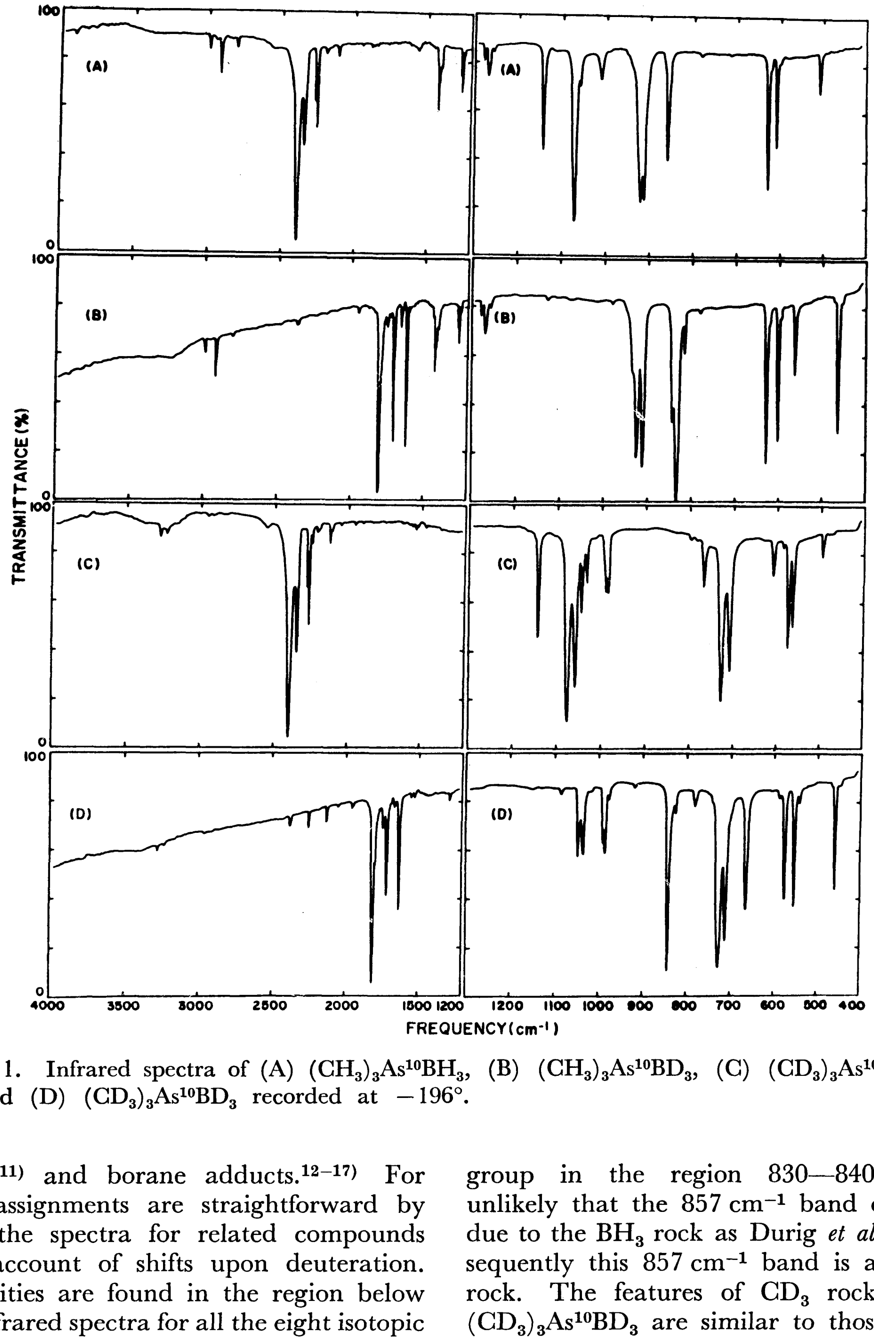

Fig. 1. Infrared spectra of (A) $(CH_3)_3As^{10}BH_3$, (B) $(CH_3)_3As^{10}BD_3$, (C) $(CD_3)_3As^{10}BH_3$, and (D) $(CD_3)_3As^{10}BD_3$ recorded at $-196°$.

tion compounds[10,11] and borane adducts.[12–17] For these vibrations, assignments are straightforward by comparison with the spectra for related compounds and taking into account of shifts upon deuteration. However, complexities are found in the region below 900 cm.$^{-1}$ The infrared spectra for all the eight isotopic compounds in this region are shown in Fig. 3. ^{10}B-^{11}B shifts are useful for assigning vibrational frequencies.

In the infrared spectrum of $(CH_3)_3As^{10}BH_3$ (Fig. 1), two absorptions are observed at 919 and 911 cm^{-1}, corresponding to 925 and 912 cm^{-1} absorptions of $(CH_3)_3As^{10}BD_3$. The E methyl rock is assigned to the higher frequency band and the A_1 rock, to the lower band. The two rocking frequencies shift on deuteration of the methyl groups to 728 and 710 cm^{-1} for $(CD_3)_3As^{10}BH_3$, and to 726 and 711 cm^{-1} for $(CD_3)_3As^{10}BD_3$.

The 857 cm^{-1} absorption in the infrared spectrum of $(CH_3)_3As^{10}BH_3$ was assigned to the BH_3 rock by Durig *et al.*[4] However, no absorption is found in the region 800—970 cm^{-1} in the spectrum of $(CD_3)_3As^{10}BH_3$. The corresponding absorption for $(CH_3)_3AsAuX$ (X=Cl, Br, I)[10] has been observed in the region 830—840 cm^{-1}. No absorption is expected from $-AsAuX$ group in the region 830—840 cm^{-1}. It is very unlikely that the 857 cm^{-1} band of $(CH_3)_3As^{10}BH_3$ is due to the BH_3 rock as Durig *et al.* assigned it. Consequently this 857 cm^{-1} band is assigned to the CH_3 rock. The features of CD_3 rocking absorptions for $(CD_3)_3As^{10}BD_3$ are similar to those of $(CH_3)_3As^{10}BH_3$ except for the shifts toward lower frequencies. The 664 cm^{-1} band of $(CD_3)_3As^{10}BD_3$ is assigned to the CD_3 rock.

No absorption is found in the 850—900 cm^{-1} region in the spectrum of $(CH_3)_3As^{10}BD_3$. The CH_3 rock of this compound is assigned to the 844 cm^{-1} band. In the spectrum of $(CD_3)_3As^{10}BH_3$ also, no absorption is observed around 660 cm^{-1}, where the CD_3 rock of $(CD_3)_3As^{10}BD_3$ was assigned. The CD_3 rock of this compound is assigned to a low frequency band at 611 cm^{-1}.

The antisymmetric BH_3 and BD_3 deformations exhibit no resolvable ^{10}B-^{11}B isotopic shift. The symmetric deformation and the rocking of BH_3 and BD_3 groups have recognizable features of a ^{10}B-^{11}B isotopic shift in the infrared spctra (Fig. 3).

The symmetric BH_3 deformation indicates a clear

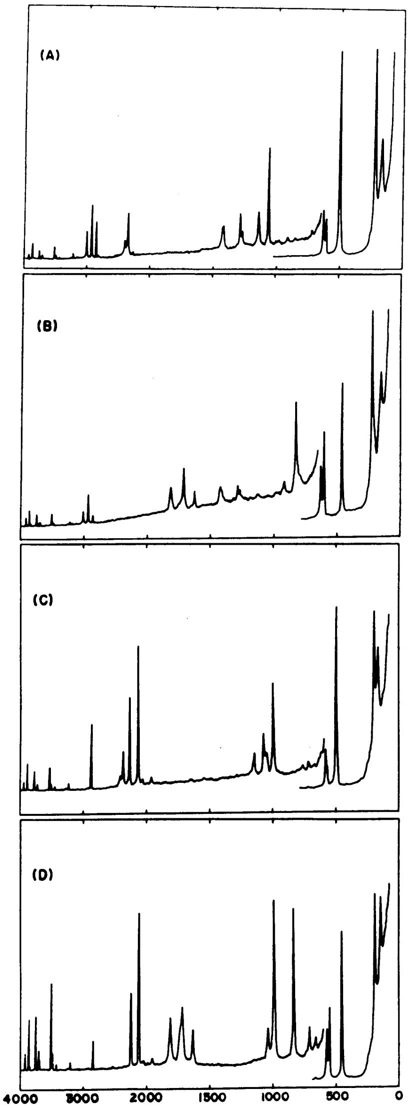

Fig. 2. Raman spectra of (A) $(CH_3)_3As^{10}BH_3$, (B) $(CH_3)_3As^{10}BD_3$, (C) $(CD_3)_3As^{10}BH_3$, and (D) $(CD_3)_3As^{10}BD_3$ recorded in the solid state at room temperature.

^{10}B-^{11}B isotopic shift at 1070 and 1060 cm^{-1} for the $(CH_3)_3As$ adduct, and at 1076 and 1065 cm^{-1} for the $(CD_3)_3As$ adduct. The infrared spectrum of $(CD_3)_3As^{10}BH_3$ represents curious features of a moderately strong absorption at 1059 cm^{-1}, which is lower by 6 cm^{-1} than the $^{11}BH_3$ symmetric deformation frequency (1065 cm^{-1}) and more intense than that expected from ^{11}B content (94% ^{10}B and 6% ^{11}B). The assignment of this absorption is still uncertain.

The symmetric BD_3 deformation for $(CD_3)_3As$ adducts are found at 842 cm^{-1} for $^{10}BD_3$ and at 827 cm^{-1} for $^{11}BD_3$. The antisymmetric BD_3 deformations are assigned to the bands at 842 cm^{-1} of the same frequency as that the symmetric $^{10}BD_3$ deformation. The symmetric BD_3 deformation for $(CH_3)_3As$ adducts is assigned to the absorption at 834 cm^{-1} for $^{10}BD_3$ and at 819 cm^{-1} for $^{11}BD_3$. Similarly the antisymmetric BD_3 deformation of $(CH_3)_3As$ adducts is assigned to the band at 834 cm^{-1} of the same frequency as the symmetric $^{10}BD_3$ deformation. We observe another

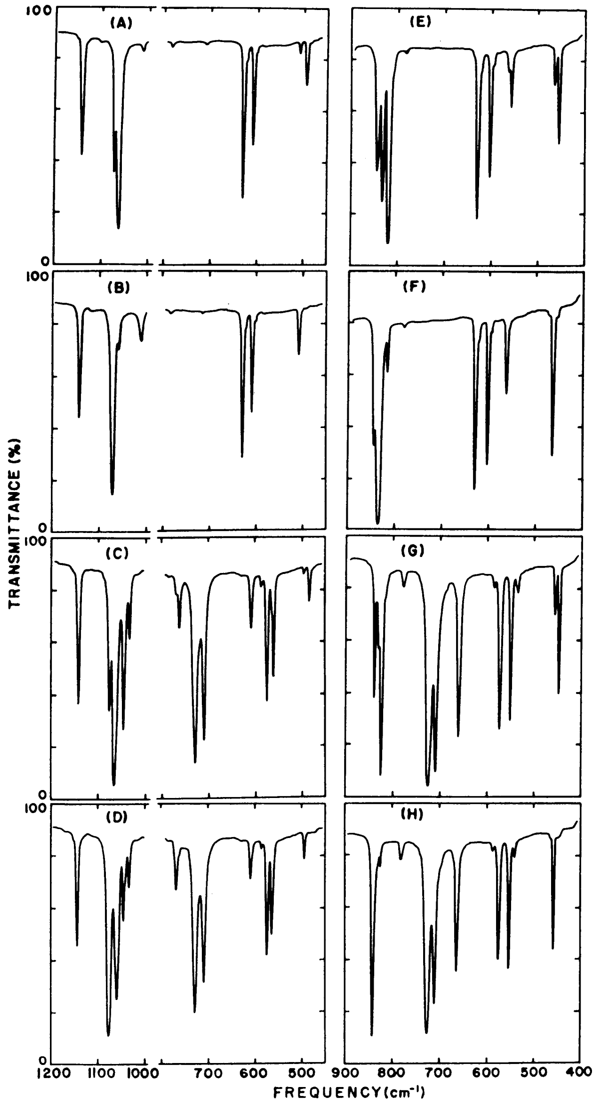

Fig. 3. Infrared spectra in the 1200—400 cm^{-1} region at −196 °. (A) $(CH_3)_3AsBH_3$, (B) $(CH_3)_3As^{10}BH_3$, (C) $(CD_3)_3AsBH_3$, (D) $(CD_3)_3As^{10}BH_3$, (E) $(CH_3)_3AsBD_3$, (F) $(CH_3)_3As^{10}BD_3$, (G) $(CD_3)_3AsBD_3$, and (H) $(CD_3)_3As^{10}BD_3$.

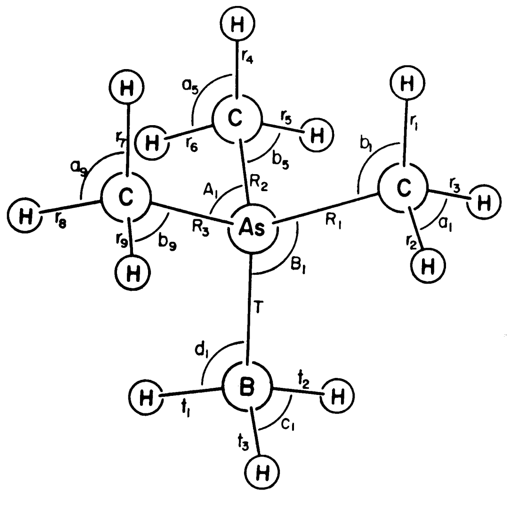

Fig. 4. Internal coordinates for trimethylarsine-borane.

absorption at 844 cm^{-1} in this region, which was previously assigned to the CH_3 rock.

A ^{10}B-^{11}B isotopic shift is also useful for the assignment of the BH_3 and BD_3 rocks. However, the rocks are rather weak and a coupling with the CH_3 or CD_3 rock makes the assignment more complicated. The $^{10}BH_3$ rock of $(CD_3)_3As^{10}BH_3$ is assigned to a band of weak intensity at 769 cm^{-1}. The $^{11}BH_3$ rocking frequency shifts by 6 cm^{-1} to 763 cm^{-1}. No absorptions assignable to the BH_3 rock are observed in the region 700—800 cm^{-1} in the infrared spectrum of $(CH_3)_3As^{10}BH_3$, but two very weak absorptions are found at 784 and 715 cm^{-1}. The latter band exhibits an isotopic shift, corresponding to the 710 cm^{-1} band for $(CH_3)_3AsBH_3$. Thus the 715 and 710 cm^{-1} bands are assigned to the $^{10}BH_3$ and $^{11}BH_3$ rocks, respectively for $(CH_3)_3AsBH_3$.

In the infrared spectrum of $(CH_3)_3As^{10}BD_3$, the 566 cm^{-1} band is assigned to the $^{10}BD_3$ rock, and the $^{11}BD_3$ rock is assigned to the 560 cm^{-1} absorption shifting by 6 cm^{-1}. For $(CD_3)_3AsBD_3$ adducts, the weak bands of low frequencies at 545 and 541 cm^{-1} are assigned to the $^{10}BD_3$ and $^{11}BD_3$ rocks, respectively.

Another absorption is observed in the region 450—500 cm^{-1} exhibiting a ^{10}B-^{11}B isotopic shift, which is assigned to the As–B stretching vibration. This vibration gives the most intense Raman band.

We should expect three skeletal deformations except the torsional modes in the region below 300 cm^{-1}. In the Raman spectra two strong Raman lines are observed. Durig *et al.*[4] resolved the higher frequency line into two at 232 and 217 cm^{-1} for $(CH_3)_3AsBH_3$, and at 232 and 216 cm^{-1} for $(CH_3)_3AsBD_3$, at liquid nitrogen temperature. We could not resolve the lines into two in either the infrared or Raman spectra under the experimental conditions. Consequently a higher frequency Raman line is assigned to the symmetric and the antisymmetric AsC_3 deformation. Finally a lower one is assigned to the AsC_3 rock which can be described as the CAsB bending mode.

One torsional mode should be observed, but no features ascribable to this mode were found in both the infrared and Raman spectra.

Normal Coordinate Analysis

Normal coordinate analysis was carried out in order to confirm the above assignments. The analysis was made by Wilson's *GF* matrix method on an ACOS 77/700 computer at the Computer Center, Tohoku

TABLE 1. SYMMETRY COORDINATES FOR TRIMETHYLARSINE-BORANE[a)]

A_1 $S_1 = (2r_1-r_2-r_3) + (2r_4-r_5-r_6) + (2r_7-r_8-r_9)$
$S_2 = (r_1+r_2+r_3) + (r_4+r_5+r_6) + (r_7+r_8+r_9)$
$S_3 = (t_1+t_2+t_3)$
$S_4 = (2a_1-a_2-a_3) + (2a_4-a_5-a_6) + (2a_7-a_8-a_9)$
$S_5 = (a_1+a_2+a_3-b_1-b_2-b_3)$
$+ (a_4+a_5+a_6-b_4-b_5-b_6)$
$+ (a_7+a_8+a_9-b_7-b_8-b_9)$
$S_6 = m(c_1+c_2+c_3) - (d_1+d_2+d_3)^{b)}$
$S_7 = (2b_1-b_2-b_3) + (2b_4-b_5-b_6) + (2b_7-b_8-b_9)$
$S_8 = (R_1+R_2+R_3)$
$S_9 = T$
$S_{10} = n(A_1+A_2+A_3) - (B_1+B_2+B_3)^{c)}$
$S_{11} = (a_1+a_2+a_3+b_1+b_2+b_3)$
$+ (a_4+a_5+a_6+b_4+b_5+b_6)$
$+ (a_7+a_8+a_9+b_7+b_8+b_9)$
$S_{12} = (c_1+c_2+c_3) + m(d_1+d_2+d_3)^{b)}$
$S_{13} = (A_1+A_2+A_3) + n(B_1+B_2+B_3)^{c)}$

A_2 $S_{14} = (r_2-r_3) + (r_5-r_6) + (r_8-r_9)$
$S_{15} = (a_2-a_3) + (a_5-a_6) + (a_8-a_9)$
$S_{16} = (b_2-b_3) + (b_5-b_6) + (b_8-b_9)$
$S_{17} = (p_1+p_2+p_3)^{d)}$
$S_{18} = p_4^{e)}$

E $S_{19} = 2(2r_1-r_2-r_3) - (2r_4-r_5-r_6) - (2r_7-r_8-r_9)$
$S_{20} = -(r_5-r_6) + (r_8-r_9)$
$S_{21} = 2(r_1+r_2+r_3) - (r_4+r_5+r_6) - (r_7+r_8+r_9)$
$S_{22} = (2t_1-t_2-t_3)$
$S_{23} = 2(2a_1-a_2-a_3) - (2a_4-a_5-a_6) - (2a_7-a_8-a_9)$
$S_{24} = -(a_5-a_6) + (a_8-a_9)$
$S_{25} = 2(a_1+a_2+a_3-b_1-b_2-b_3)$
$- (a_4+a_5+a_6-b_4-b_5-b_6)$
$- (a_7+a_8+a_9-b_7-b_8-b_9)$
$S_{26} = (2c_1-c_2-c_3)$
$S_{27} = 2(2b_1-b_2-b_3) - (2b_4-b_5-b_6)$
$- (2b_7-b_8-b_9)$
$S_{28} = -(b_5-b_6) + (b_8-b_9)$
$S_{29} = (2d_1-d_2-d_3)$
$S_{30} = (2R_1-R_2-R_3)$
$S_{31} = (2A_1-A_2-A_3)$
$S_{32} = (2B_1-B_2-B_3)$
$S_{33} = -(p_2-p_3)^{d)}$
$S_{34} = 2(a_1+a_2+a_3+b_1+b_2+b_3)$
$- (a_4+a_5+a_6+b_4+b_5+b_6)$
$- (a_7+a_8+a_9+b_7+b_8+b_9)$

E $S_{35} = (2r_4-r_5-r_6)-(2r_7-r_8-r_9)$
$S_{36} = 2(r_2-r_3) - (r_5-r_6) - (r_8-r_9)$
$S_{37} = (r_4+r_5+r_6) - (r_7+r_8+r_9)$
$S_{38} = (t_2-t_3)$
$S_{39} = (2a_4-a_5-a_6) - (2a_7-a_8-a_9)$
$S_{40} = 2(a_2-a_3) - (a_5-a_6) - (a_8-a_9)$
$S_{41} = (a_4+a_5+a_6-b_4-b_5-b_6)$
$- (a_7+a_8+a_9-b_7-b_8-b_9)$
$S_{42} = (c_2-c_3)$
$S_{43} = (2b_4-b_5-b_6) - (2b_7-b_8-b_9)$
$S_{44} = 2(b_2-b_3) - (b_5-b_6) - (b_8-b_9)$
$S_{45} = (d_2-d_3)$
$S_{46} = (R_2-R_3)$
$S_{47} = (A_2-A_3)$
$S_{48} = (B_2-B_3)$
$S_{49} = (2p_1-p_2-p_3)^{d)}$
$S_{50} = (a_4+a_5+a_6+b_4+b_5+b_6)$
$- (a_7+a_8+a_9+b_7+b_8+b_9)$

a) Normalization factors are omitted. b) $m=-\sqrt{3}\cos(d)/\cos(c/2)$. c) $n=-\sqrt{3}\cos(B)/\cos(A/2)$. d) The CH_3 torsions are p_1, p_2, and p_3. e) The BH_3 torsion is p_4.

TABLE 2. VIBRATIONAL NUMBERS FOR THE FUNDAMENTALS OF TRIMETHYLARSINE-BORANE[a)]

Vibrational mode	Number		
	A_1	A_2	E
Stretching $(CH_3)_a$ or $(CD_3)_a$	1	11	16, 17
Stretching $(CH_3)_s$ or $(CD_3)_s$	2		18
Stretching (BH_3) or (BD_3)	3		19
Deformation $(CH_3)_a$ or $(CD_3)_a$	4	12	20, 21
Deformation $(CH_3)_s$ or $(CD_3)_s$	5		22
Deformation (BH_3) or (BD_3)	6		23
Rocking (CH_3) or (CD_3)	7	13	24, 25
Rocking (BH_3) or (BD_3)			26
Stretching (AsC_3)	8		27
Stretching (AsB)	9		
Deformation (AsC_3)	10		28
Rocking (AsC_3)			29
Torsion (CH_3) or (CD_3)		14	30
Torsion (BH_3) or (BD_3)		15	

a) Abbreviations used: a, antisymmetric; s, symmetric.

TABLE 3. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CH_3)_3As^{10}BH_3$[a)]

No.	Infrared solid	Raman solid	Raman solution	Calcd	PED[b)]
1	2994 w	3001 m		3002	$100F_1$
2	2919 m	2921 m	2924 m, p	2920	$94F_2$
3	2346 m	2350 m	2350 m, p	2347	$88F_3$
4	1427 w	1419 m		1430	$94F_4$
5	1278 w	1289 m	1286 m, p	1280	$86F_5, 13F_2$
6	1070 s	1067 s	1069 m, p	1074	$79F_6, 17F_3$
7	911 s	912 vw	900 w	919	$92F_7$
8	610 m	609 m	606 s, p	613	$83F_8, 13F_9$
9	510 w	506 vs	498 m, p	518	$83F_9, 14F_8$
10		226 vs	219 s	224	$97F_{10}$
16	2994 w	3001 m		3002	$78F_{16}, 22F_{17}$
17	2994 w	3001 m		3001	$78F_{17}, 22F_{16}$
18	2919 m	2921 m	2924 m	2922	$95F_{18}$
19	2393 s	2401 m	2402 s	2397	$99F_{19}$
20	1433 m	1431 m		1439	$94F_{20}$
21	1427 w			1429	$96F_{21}$
22	1269 m	1279 w	1269 m	1275	$88F_{22}$
23	1141 m	1144 m	1144 m	1146	$97F_{23}$
24	919 s	917 vw	900 w	930	$79F_{24}$
25	857 m	859 vw	854 vw	862	$67F_{25}, 15F_{26}$
26	715 vw	721 vw		725	$73F_{26}, 25F_{25}$
27	629 s	630 m	626 m	640	$85F_{27}, 13F_{24}$
28		226 vs	219 s	225	$96F_{28}$
29		175 m	166 s	173	$97F_{29}$

a) Abbreviations: v, very; w, weak; m, medium; s, strong; p, polarized. b) Values less than 10% in magnitude are omitted.

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CH_3)_3As^{10}BD_3$[a)]

No.	Infrared solid	Raman solid	Raman solution	Calcd	PED[b)]
1	2994 w	3001 w		3002	$100F_1$
2	2920 m	2921 m	2924 m, p	2920	$94F_2$
3	1715 s	1715 m	1714 s, p	1717	$81F_3$
4	1425 w	1417 w		1430	$94F_4$
5	1278 w	1289 w	1286 m, p	1280	$86F_5, 10F_2$
6	834 s	827 m	827 s, p	836	$68F_6, 20F_3, 11F_9$
7	912 s	920 vw	917 w	919	$92F_7$
8	606 s	604 m	601 vs, p	608	$91F_8$
9	469 s	465 s	458 m, p	466	$78F_9$
10		226 s	219 s	223	$96F_{10}$
16	2994 w	3001 w		3002	$78F_{16}, 22F_{17}$
17	2994 w	3001 w		3001	$78F_{17}, 22F_{16}$
18	2920 m	2921 m	2924 m	2922	$95F_{18}$
19	1816 s	1815 m	1816 m	1809	$98F_{19}$
20	1434 m			1439	$94F_{20}$
21	1427 w	1428 w		1428	$96F_{21}$
22	1270 w	1270 w	1267 m	1275	$88F_{22}$
23	834 s	827 m	827 s	831	$84F_{23}, 13F_{25}$
24	925 s	920 vw		929	$80F_{24}$
25	844 m			844	$75F_{25}, 13F_{23}$
26	566 m	565 vw		551	$97F_{26}$
27	632 s	630 m	627 m	642	$85F_{27}, 13F_{24}$
28		226 s	219 s	224	$96F_{28}$
29		158 m	151 s	160	$96F_{29}$

a) For abbreviations, see Table 3.
b) Values less than 10% in magnitude are omitted.

University, by means of the usual iterative least-squares procedure.

The 50 symmetry coordinates (Table 1) were constructed from the 50 internal coordinates (Fig. 4). The symmetry coordinates are mutually orthonormal, and by using them the *G* matrix is completely broken into a 10 by 10, a 5 by 5, two 15 by 15 matrices and 5 redundancies, not including non-zero cross terms between any two symmetry blocks. The corresponding terms of two degenerate pairs are equal to each other. In constructing the symmetry coordinates of C_{3v} $(XY_3)_3Z$ group, those of Kuroda and Kimura[18)] were often used. Care should be taken so that the matrix is completely broken into the symmetry blocks, and for the degenerate symmetry species in particular, each element of a matrix must be equal to the corresponding one of another degenerate pair.

The *G* matrix was calculated by use of the structural parameters determined from the microwave study[4)] assuming tetrahedral angle around carbon atoms: $r(C–H)=1.09$ Å, $r(B–H)=1.212$ Å, $r(As–C)=1.945$ Å, $r(As–B)=2.035$ Å, $\angle(HBH)=113.5°$, and $\angle(CAsC)=105°$.

In the calculations the infrared frequencies were used except for the AsC_3 deformation for which the Raman frequencies were taken and the observed frequencies were weighted by $(1/\lambda)$. Initial force constants for the borane group were taken from the values by Durig *et al.*,[4)] and for trimethylarsine moiety, from those for trimethylarsine oxide.[5)]

The least-squares refinement was carried out in terms of symmetry force constants, which were fitted to the observed frequencies for four ^{10}B compounds simultaneously.

The observed and calculated frequencies are given

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CD_3)_3As^{10}BH_3$[a)]

No.	Infrared solid	Raman solid	Raman solution	Calcd	PED[b)]
1	2248 w	2252 s	2252 m	2238	$98F_1$
2	2127 w	2129 s	2131 s, p	2126	$99F_2$
3	2346 m	2351 m	2351 m, p	2347	$88F_3$
4	1034 m	1039 m	1037 m	1031	$96F_4$
5	989 m	995 s	992 vs, p	987	$75F_5, 13F_2, 11F_8$
6	1076 s	1071 m	1070 m, p	1074	$79F_6, 17F_3$
7	710 s	712 w		701	$89F_7$
8	567 m	565 m	561 m, p	564	$47F_8, 38F_9$
9	499 w	496 vs	487 s, p	501	$56F_9, 37F_8$
10		197 s	188 s	200	$95F_{10}$
16	2248 w	2252 s	2252 m	2238	$51F_{16}, 47F_{17}$
17	2248 w	2252 s	2252 m	2236	$51F_{17}, 47F_{16}$
18	2127 w	2129 s	2131 s	2124	$91F_{18}$
19	2392 s	2400 w	2400 w	2397	$99F_{19}$
20	1046 m	1054 m	1037 m	1038	$93F_{20}$
21	1034 m	1044 m	1037 m	1033	$95F_{21}$
22	984 m	990 sh	986 sh	978	$75F_{22}, 12F_{27}, 10F_{18}$
23	1143 m	1144 w	1144 m	1146	$97F_{23}$
24	728 s	712 w		712	$59F_{24}, 12F_{27}$
25	611 w	614 vw		614	$79F_{25}, 16F_{26}$
26	769 w	763 w		777	$76F_{26}$
27	577 m	576 w	573 m	564	$60F_{27}, 28F_{24}$
28		197 s	188 s	197	$93F_{28}$
29		169 m	157 s	166	$97F_{29}$

a) Abbreviations: sh, shoulder. For the others, see Table 3.

b) Values less than 10% in magnitude are omitted.

TABLE 6. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CD_3)_3As^{10}BD_3$[a)]

No.	Infrared solid	Raman solid	Raman solution	Calcd	PED[b)]
1	2248 w	2251 m	2251 m	2238	$98F_1$
2	2128 w	2128 s	2129 vs, p	2126	$90F_2$
3	1720 m	1718 m	1723 m, p	1717	$81F_3$
4	1035 m	1035 m	1035 m	1031	$96F_4$
5	990 m	995 s	992 vs, p	987	$75F_5, 13F_2, 11F_8$
6	842 s	838 s	835 s, p	837	$67F_6, 20F_3, 11F_9$
7	711 s	713 w		700	$90F_7$
8	556 m	555 m	553 s, p	551	$71F_8, 11F_9$
9	463 m	457 s	451 s, p	459	$71F_9, 13F_8$
10		195 m	188 s	199	$95F_{10}$
16	2248 w	2251 m	2251 m	2238	$51F_{16}, 47F_{17}$
17	2248 w	2251 m	2251 m	2236	$51F_{17}, 47F_{16}$
18	2128 w	2128 s	2129 vs	2124	$91F_{18}$
19	1815 s	1813 m	1816 m	1809	$98F_{19}$
20	1048 m	1041 m	1035 m	1038	$93F_{20}$
21	1035 m	1035 m	1035 m	1032	$95F_{21}$
22	985 m	988 sh	985 sh	978	$75F_{22}, 12F_{27}, 10F_{18}$
23	842 s	838 s	835 s	833	$97F_{23}$
24	726 s	713 w		720	$53F_{24}, 16F_{27}$
25	664 w	663 w	662 w	652	$62F_{25}, 13F_{24}, 13F_{26}$
26	545 w			539	$75F_{26}, 21F_{25}$
27	578 m	576 m	573 m	565	$62F_{27}, 29F_{24}$
28		195 m	188 s	197	$94F_{28}$
29		150 m	142 s	152	$96F_{29}$

a) Abbreviations: sh, shoulder. For the others, see Table 3.

b) Values less than 10% in magnitude are omitted.

in Tables 3—6 for four ^{10}B isotopic species, in which the vibrational numbers refer to the vibrational modes (Table 2). The calculated frequencies have an average error of 0.52% for A_1 vibrations and 0.74% for E vibrations. The sum of the weighted squares of errors $\Sigma(\lambda_{obsd}-\lambda_{calcd})^2/\lambda_{obsd}$ was 2.24×10^{-3} for A_1 and 7.02×10^{-3} for E. The symmetry force constants together with the uncertainty from the last cycle of the least-squares refinement are given in Table 7. The observed frequencies of the ^{11}B compounds together with the frequencies calculated by use of the force constants (Table 7) are given in Table 8.

Discussion

As seen in the potential energy distributions, the BH_3 and BD_3 rocks couple with the CH_3 and CD_3 rocks, making the rocking frequency region complicated.

The valence force constants obtained from the symmetry force constants are compared with those of other borane and related compounds (Table 9). The force constant f_{N-B} of H_3NBH_3 is greater than that of $(CH_3)_3NBH_3$, whereas the force constant f_{P-B} of H_3PBH_3 is smaller than that of $(CH_3)_3PBH_3$. Arsine, AsH_3, forms no addition compound with borane. If arsine could form a borane adduct, f_{As-B} of arsine–borane would be smaller than 1.849 mdyn/Å obtained for

TABLE 7. SYMMETRY FORCE CONSTANTS AND THEIR UNCERTAINTIES FOR TRIMETHYLARSINE–BORANE[a)]

		σ			σ
F_1	4.790	0.011	F_{16}	4.792	0.028
F_2	4.736	0.054	F_{17}	4.791	0.028
F_3	2.983	0.047	F_{18}	4.762	0.079
F_4	0.516	0.003	F_{19}	2.973	0.013
F_5	0.532	0.016	F_{20}	0.523	0.004
F_6	0.583	0.021	F_{21}	0.520	0.004
F_7	0.575	0.005	F_{22}	0.534	0.022
F_8	2.924	0.038	F_{23}	0.383	0.004
F_9	1.849	0.039	F_{24}	0.575	0.016
F_{10}	0.605	0.018	F_{25}	0.473	0.009
			F_{26}	0.465	0.009
$F_{2,5}$	−0.385	0.066	F_{27}	3.169	0.125
$F_{3,6}$	−0.442	0.048	F_{28}	0.713	0.030
$F_{5,8}$	−0.170	0.033	F_{29}	0.383	0.021
$F_{6,9}$	−0.159	0.030			
			$F_{18,22}$	−0.356	0.101
			$F_{22,27}$	−0.265	0.045
			$F_{24,27}$	−0.264	0.049
			$F_{25,26}$	0.065	0.007

a) The stretching force constants are given in mdyn/Å, the deformation force constants in mdyn Å, the stretching-deformation interaction constants in mdyn.

Table 8. Observed and calculated frequencies (cm^{-1}) for ^{11}B isotopic species$^{a)}$

No.	Observed (infrared)				Calculated			
	$(CH_3)_3As$		$(CD_3)_3As$		$(CH_3)_3As$		$(CD_3)_3As$	
	$^{11}BH_3$	$^{11}BD_3$	$^{11}BH_3$	$^{11}BD_3$	$^{11}BH_3$	$^{11}BD_3$	$^{11}BH_3$	$^{11}BD_3$
1	2995	2993	2248	2249	3002	3002	2238	2238
2	2920	2918	2128	2127	2920	2920	2126	2126
3	2346	1701	2346	1700	2340	1706	2340	1706
4	1427	1427	1034	1035	1430	1430	1031	1031
5	1279	1278	989	990	1280	1280	987	987
6	1060	819	1065	827	1065	823	1065	823
7	913	913	710	711	919	919	701	700
8	610	606	564	556	612	608	559	550
9	497	459	488	454	504	458	490	451
10	226	225	198	196	224	223	200	199
16	2995	2993	2248	2249	3002	3002	2238	2238
17	2995	2993	2248	2249	3002	3002	2236	2236
18	2920	2918	2128	2127	2922	2922	2124	2124
19	2380	1797	2382	1797	2383	1788	2383	1788
20	1433	1433	1046	1047	1439	1439	1038	1038
21	1427	1425	1035	1035	1429	1428	1033	1032
22	1270	1269	985	984	1275	1275	978	978
23	1140	834	1141	842	1143	827	1143	830
24	921	927	729	726	930	929	713	720
25	858	844	612	663	861	844	614	651
26	710	560	763	541	722	548	773	536
27	631	631	578	578	640	642	564	565
28	226	225	198	196	225	225	197	197
29	173	155	165	147	171	159	163	151

a) The force constants in Table 7 were used in frequency calculations. Observed frequencies for the vibrational number 10, 28, and 29 are taken from the Raman spectra.

Table 9. Comparison of the valence force constants (mdyn/Å) for the borane addition compounds (X=N, P, As)

	f_{B-X}	f_{As-C}	f_{B-H}	Ref.
H_3NBH_3	2.90		2.88	19
$(CH_3)_3NBH_3$	2.36		2.7	19
	2.59		2.49	13
F_3PBH_3	2.39			20
H_3PBH_3	1.78			15
	1.97		3.10	21
$CH_3PH_2BH_3$	2.44		3.07	14
$(CH_3)_3PBH_3$	2.37		2.987	12
$(CH_3)_3AsBH_3$	1.84	2.97	3.06	4
	1.849	3.087	2.976	This work
$(CH_3)_3AsO$		3.099		5
$(CH_3)_3As$		2.56		4, 22
		2.63		23

$(CH_3)_3AsBH_3$. As expected the stability of trimethylarsine–borane is less than that of N and P analogs. The trend is reflected in the stretching force constants of the donor-acceptor bonds.

The CAsC angle becomes larger by adduct formation toward the tetrahedral angle and s character increases in rehybridization around the arsenic atom. This accounts for the increase in the As–C force constant and in the As–C stretching frequencies.

The As–B force constant is in good agreement with the value obtained by Durig *et al.*,$^{4)}$ the f_{As-C} value being slightly larger than theirs, but in accord with that in $(CH_3)_3AsO$. The B–H force constant is larger than that in amine–boranes, but smaller than that in phosphine–boranes. Accurate examination for other boranes would be necessary in order to compare the B–H force constant with the value obtained in this study.

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