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Microwave, Infrared, Raman, and Nuclear Magnetic Resonance Spectra and Structure of Trimethylarsine-Borane

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The infrared (33-4000 cm^{-1}) and Raman (0-3500 cm^{-1}) spectra of $(CH_3)_3As·BH_3$ and $(CH_3)_3As·BD_3$ have been recorded for the solid state at low temperature. The spectra have been interpreted in detail on the basis of C_{3v} molecular symmetry. The valence force field model has been utilized in calculating the frequencies and potential energy distribution. A normal-coordinate analysis of $(CH_3)_3As$ was calculated to obtain VFF force constants for comparison with the force constants of the adduct and the differences are shown to be consistent with the structural changes found upon adduct formation. The As-B stretch was found to be mixed with the As-C stretch. The As-B force constant was found to have a value of 1.84 mdyn/Å which seems to be consistent with the adduct stability. The microwave spectra of $(CH_3)_3As·{}^{11}BH_3$, $(CH_3)_3As·{}^{10}BH_3$, $(CH_3)_3As·{}^{11}BD_3$, and $(CH_3)_3As·{}^{10}BD_3$ were recorded from 26.5 to 40 GHz. With reasonable assumptions for the BH_3 and CH_3 structural parameters *r*(As-B), *r*(As-C), and ∠CAsB were found to have the following values: 2.035 Å, 1.945 Å, and 113°. These parameters are compared to the corresponding ones for the Lewis base and are shown to be consistent with changes expected with adduct formation. Nuclear magnetic resonance parameters are also reported for the $(CH_3)_3$-$As·BH_3$ molecule.

Introduction

The discovery[2] of the exceedingly stable boron-phosphorus trimers and tetramers based on the $[(CH_3)_2PBH_2]_n$ and $[(CH_3)_2PB(CH_3)_2]_n$ units (where $n = 3, 4$) led to the question of whether analogous boron-arsenic compounds would have the same unexpected stability. In a study[3] of arsenic-boron bonding, Stone and Burg reported the preparation and properties of several arsine-boranes and arsinoborine polymers. It was found that As-B compounds were similar to the corresponding P-B compounds except that the bonds involving arsenic were weaker than those of the corresponding phorphorus adducts.

In view of our interest in group IIIa-group Va addition compounds[4,5] and in the structural parameters of B-P adducts in particular,[6] it was felt that a comparison of the corresponding parameters in arsine-boranes would be useful. No gas-phase structural work has been reported for this class of compounds. Detailed vibrational studies are also completely lacking. Thus, we report herein an infrared, Raman, and microwave study of the trimethylarsine-borane molecule.

Experimental Section

All preparative work was carried out in a conventional high-vacuum system employing greaseless stopcocks. Trimethylarsine was obtained commercially (Strem Chemical Co.),and purified by trap-to-trap distillation. Diborane(6) was prepared by the addition of potassium borohydride to hot polyphosphoric acid[7] and deuteriodiborane(6) was prepared in a similar manner using $NaBD_4$.

Trimethylarsine-borane species were prepared by condensing $(CH_3)_3As$ and B_2H_6 in a 2:1 mole ratio into a 50-ml Pyrex tube fitted with a greaseless stopcock. The tube was isolated from the vacuum system by closing the stopcock and was allowed to warm slowly to room temperature. After 1 hr, the tube was immersed in a 0° bath and opened to the system to remove traces of unreacted $(CH_3)_3As$ and/or B_2H_6. To monitor purity, a sample of $(CH_3)_3As·BH_3$ was transferred under vacuum into a 5-mm nmr tube. Carbon disulfide was condensed onto the sample and the tube flame-sealed from the vacuum system. A ^{11}B nmr spectrum was obtained at ambient temperature on a Varian Associates XL-100-15 nmr spectrometer operating 32.1 MHz. Field-frequency lock was provided by an external ^{19}F source. The ^{11}B spectrum consisted of a quartet with lines of 1:3:3:1 relative intensity and exhibited a J_{B-H} value of 100 Hz. The chemical shift of this resonance was found to be 50.5 ppm shielded with respect to an external sample of $B(OCH_3)_3$. A proton noise-decoupled spectrum of this sample exhibited a single line with no observable arsenic-boron spin-spin coupling.

The microwave spectra were obtained with a Hewlett-Packard Model 8460A MRR spectrometer with 33.33-kHz square-wave Stark modulation. The Stark cells were cooled to −20° and the sample pressure held to about 15 μ. The line frequencies were measured at slow scan rates and the accuracy in the measurements is better than 0.5 MHz. The adduct was observed to dissociate slowly at −20° in the wave guide requiring the sample to be renewed every 20-30 min.

The Raman spectra were recorded from 0 to 3500 cm^{-1} using a Cary Model 82 Raman spectrophotometer equipped with a Coherent Radiation Model 52-A argon ion laser. The Raman spectrophotometer was calibrated with the emission lines of neon.The sample was allowed to sublime slowly onto a blackened brass block in thermal contact with a reservoir of boiling liquid nitrogen. The design of the Raman low-temperature cell has been described[8] previously.

A Perkin-Elmer Model 621 infrared grating spectrophotometer, which was purged with dry nitrogen and calibrated in the usual manner, was used to record the spectra of $(CH_3)_3As·BH_3$ and $(CH_3)_3As·BD_3$ from 4000 to 250 cm^{-1}. The spectra were recorded with the sample which had been deposited on a CsI plate mounted in a brass block in thermal contact with a reservoir of boiling liquid nitrogen. The low-temperature cell used has been described[8] elsewhere.

The far-infrared spectra were recorded between 33 and 350 cm^{-1} with a Beckman IR-11 double-beam grating spectrophotometer which was purged with dry nitrogen. The instrument was calibrated with water vapor frequencies. The sample was allowed to sublime slowly onto a silicon substrate which was contained in a low-temperature cell similar to the one used in both the Raman and mid-infrared study.

Microwave Results

The observed transitions, the rotational constants, and the moments of inertia for $(CH_3)_3As·{}^{11}BH_3$, $(CH_3)_3As·{}^{10}BH_3$, $(CH_3)_3As·{}^{11}BD_3$, and $(CH_3)_3As·{}^{10}BD_3$ are listed in Table I. In Figure 1 the R-band microwave spectrum of $(CH_3)_3As·BH_3$ is shown. The 5 ← 4, 6 ← 5, and 7 ← 6 rotational transition of the $(CH_3)_3As·{}^{11}BH_3$ isotopic species are the most intense features in the spectrum. The 6 ← 5 transition of

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[1] Taken in part from the thesis of B. A. Hudgens to be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

[2] A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, **75**, 3872 (1953).

[3] F. G. A. Stone and A. B. Burg, *J. Amer. Chem. Soc.*, **76**, 386 (1954).

[4] J. D. Odom, J. A. Barnes, and B. A. Hudgens, submitted for publication in *J. Phys. Chem.*

[5] J. R. Durig, Y. S. Li, and J. D. Odom, *J. Mol. Struct.*, **16**, 443 (1973).

[6] J. D. Odom, B. A. Hudgens, and J. R. Durig, *J. Phys. Chem.*, **77**, 1972 (1973).

[7] A. D. Norman and W. L. Jolly, *Inorg. Syn.*, **11**, 15 (1968).

[8] F. G. Baglin, S. F. Bush, and J. R. Durig, *J. Chem. Phys.*, **47**, 2104 (1970).

Table I. Ground-State Transitions (MHz), Rotational Constants (MHz), and Moments of Inertia (amu Å^2)^a of Four Symmetric Tops of Trimethylarsine-Borane

Species	$5 \leftarrow 4$	$6 \leftarrow 5$	$7 \leftarrow 6$	B	I_b
$(CH_3)_3As\cdot{}^{11}BH_3$	28,379.70	34,055.64	39,731.53	2837.97	178.007
$(CH_3)_3As\cdot{}^{10}BH_3$	29,092.31	34,910.77		2909.23	173.715
$(CH_3)_3As\cdot{}^{11}BD_3$		30,809.16	35,944.02	2567.43	196.840
$(CH_3)_3As\cdot{}^{10}BD_3$		31,478.51	36,724.93	2623.21	192.656

[a] Conversion factor 505377 amu Å^2/MHz.

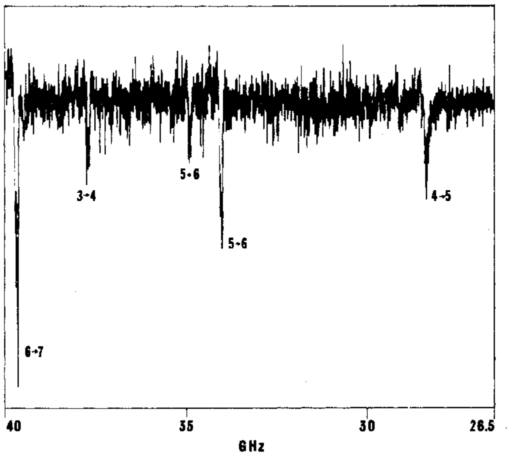

Figure 1. The R-band microwave spectrum of $(CH_3)_3As\cdot BH_3$.

the $(CH_3)_3As\cdot{}^{10}BH_3$ isotopic species, which is approximately one-fourth as intense as the same transition for the ^{11}B isotopic species, is shown on the high-frequency side of the ^{11}B transition. Trimethylarsine-borane slowly dissociates in the gas phase and the $4 \leftarrow 3$ transition of trimethylarsine is labeled in Figure 1. In Figure 2 is shown a higher resolution scan of the $7 \leftarrow 6$ transition of $(CH_3)_3As\cdot{}^{11}BH_3$. The ground-state line is the most intense line. The excited-state lines of the six modes falling below 250 cm^{-1} are observed to occur on both sides of the ground-state line. No evidence of quadrupole splitting was observed.

In an attempt to fit the structure of $(CH_3)_3As\cdot BH_3$ to the four observed moments of inertia the structural parameters of the methyl and borane groups were assumed. A C-H bond length of 1.09 Å and a ∠HCH angle of 107°, which were used for the methyl top, are the same values assumed by Lide[9] in the structural determination of trimethylarsine. The values for the B-H bond distance of 1.212 Å and the ∠HBH bond angle of 113.5° were taken from the microwave structure of trimethylphosphine-borane.[10] The values of the As-B bond length, the As-C bond length, and the ∠CAsB bond angle were varied to fit the four observed moments of inertia. When the As-B bond length, the As-C bond length, and the ∠CAsB bond angle were taken to be 2.035 Å, 1.945 Å, and 113.0°, respectively, the observed rotational constants were calculated to within 5 MHz (see Table II).

Due to the presence of excited-state lines for the six low-frequency vibrational modes, a suitable Stark component from which the dipole moment could be determined was not found.

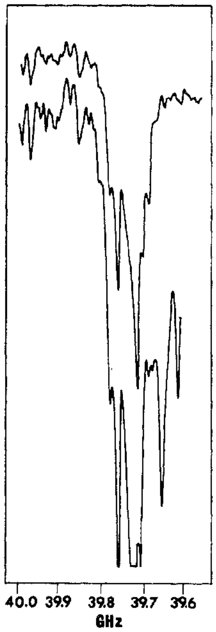

Figure 2. The $7 \leftarrow 6$ rotational transition of $(CH_3)_3As\cdot BH_3$.

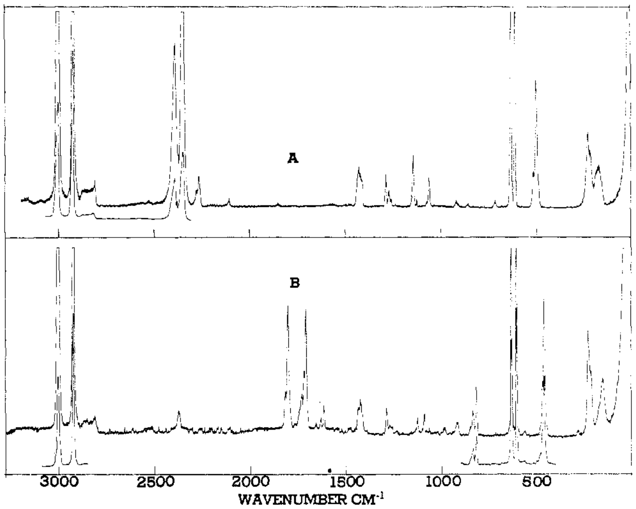

Figure 3. Raman spectra of $(CH_3)_3As\cdot BH_3$ (A) and $(CH_3)_3As\cdot BD_3$ (B) recorded at −196°.

Table II. Structural Parameters of Trimethylarsine and Trimethylarsine-Borane

Parameter	$(CH_3)_3As^a$	$(CH_3)_3As\cdot BH_3$
r(CH),^{b} Å	1.090	1.090
∠HCH,^{b} deg	107	107
r(BH),^{b} Å		1.212
∠HBH,^{b} deg		113.5
r(AsC), Å	1.959 ± 0.01	1.945
∠CAsC, deg	96 ± 3^b	105
r(AsB), Å		2.035

[a] Taken from ref 9. [b] Assumed value.

Vibrational Results

The Raman and infrared spectra of $(CH_3)_3As\cdot BH_3$ and $(CH_3)_3As\cdot BD_3$ are shown in Figures 3-5. A molecular symmetry of C_{3v}, with the C_3 axis coincident with the As-B bond, and "local" C_3 symmetry for the methyl tops are assumed for trimethylarsine-borane. From group theory, one predicts the molecule to have 10 A_1, 5 A_2, and 15 E

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(9) D. R. Lide, *Spectrochim. Acta*, 15, 473 (1959).

(10) P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, 11, 553 (1972).

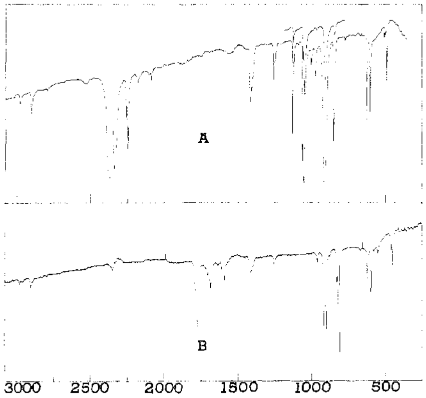

Figure 4. Mid-infrared spectra of $(CH_3)_3As{\cdot}BH_3$ (A) and $(CH_3)_3As{\cdot}BD_3$ (B) recorded at −196°.

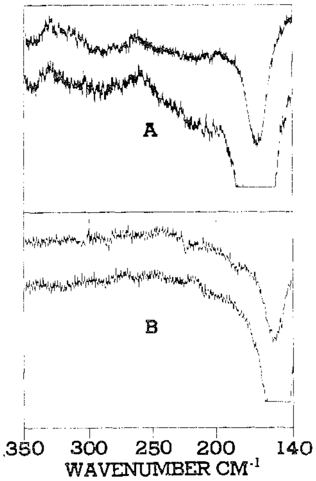

Figure 5. Far-infrared spectra of $(CH_3)_3As{\cdot}BH_3$ (A) and $(CH_3)_3As{\cdot}BD_3$ (B) recorded at −196°.

modes. The five "silent" A_2 modes are not observed even in the solid state.

CH_3 Modes. The methyl stretching region is observed to be the same as in the Lewis base[11] having all three antisymmetric CH_3 stretching modes (ν_1, ν_{16}, and ν_{17}) contained within the evelope of a single, strong Raman band at 2993 cm^{-1}. Both of the symmetric CH_3 stretches (ν_2 and ν_{18}), which are observed to be accidentally degenerate, are assigned to a very intense Raman band at 2923 cm^{-1}. The methyl stretches in the infrared spectrum are much less intense than the corresponding modes in the Raman spectrum and, indeed, are very much less intense than the same modes in the infrared spectrum of the Lewis base.[11]

The antisymmetric CH_3 deformations form a broad absorption between 1400 and 1435 cm^{-1} with a maximum at 1422 cm^{-1} and shoulders at 1430, 1414, and 1405 cm^{-1}. The maxima at 1430 and 1414 cm^{-1} are assigned to the two antisymmetric deformations of E symmetry, ν_{20} and ν_{21}. The shoulder at 1414 cm^{-1} is assigned to the A_1 antisymmetric deformation, ν_4. The frequencies of the three antisymmetric deformations do not change appreciably with the formation of the adduct.

As was observed[11] in $(CH_3)_3As$ the A_1 symmetric CH_3 deformation is assigned to a higher frequency mode than the E symmetric CH_3 deformation. A band at 1285 cm^{-1}, which is observed only in the Raman spectrum, is assigned to the A_1 symmetric CH_3 deformation. The symmetric CH_3 deformation of E symmetry is assigned to an infrared band at 1265 cm^{-1}. Each of the bands assigned to these symmetric CH_3 deformations is the strongest band in this region. An explanation as to why these modes exhibit mutual exclusion is not readily apparent.

In the infrared spectrum of $(CH_3)_3As{\cdot}BH_3$, the three methyl rocks are assigned to a single, very strong, broad band at 912 cm^{-1}. In the infrared spectrum of the deuterated species $(CH_3)_3As{\cdot}BD_3$ the single intense band in the d_0 spectrum resolves into a broad band with two distinct maxima at 925 and 910 cm^{-1}. In the Raman spectrum of the "light" compound, the CH_3 rocks are assigned to two weak bands at 923 and 909 cm^{-1} which, on deuteration of the borane groups, become a single broad, weak band at 918 cm^{-1}. The A_1 CH_3 rock and one E methyl rock are assigned to the higher frequency band and the remaining E methyl rock is assigned to the lower frequency band.

The AsC_3 stretching vibrations are assigned to two strong, sharp Raman bands. The antisymmetric AsC_3 stretching mode, which is more intense than the corresponding symmetric stretching motion in the infrared spectrum but is the less intense mode in the Raman spectrum, is observed at 630 cm^{-1} in the spectra of both the $(CH_3)_3As{\cdot}BH_3$ and $(CH_3)_3As{\cdot}BD_3$ molecules. The symmetric AsC_3 stretch is coupled with the As–B stretching mode. As a result, on deuteration of the borane group, the symmetric AsC_3 stretching mode shifts from 609 to 605 cm^{-1}.

In contrast to the behavior displayed by the skeletal deformations of the Lewis base in trimethylamine-borane[4] and trimethylphosphine-borane,[6] the AsC_3 deformations are observed at a lower frequency in the adduct than in the Lewis base. The symmetric AsC_3 deformation is assigned to a Raman line of medium intensity at 232 cm^{-1} and the antisymmetric AsC_3 deformation is assigned to a shoulder at 217 cm^{-1} on the lower frequency side of the symmetric motion. Both deformations are observed only in the Raman spectrum. The $\angle$CAsB bending mode, which may also be described as the AsC_3 rock, is observed in both the Raman and infrared spectra. The band at 166 cm^{-1} in the far-infrared spectrum of the "light" compound, which shifts to 151 cm^{-1} in the spectrum of $(CH_3)_3As{\cdot}BD_3$, is assigned to this bending motion.

As was noted for the AsC_3 stretching modes the same intensity relationship exists between the antisymmetric and symmetric BH_3 stretches in the infrared and Raman spectra of the "light" compound. In the "light" compound the bands in both the Raman and the infrared spectra are broad and show no resolvable ^{10}B–^{11}B isotopic shift; however, in the deuterated compound the bands in both the Raman and the infrared spectra are sharper and ^{10}B–^{11}B splitting is observed. The antisymmetric BH_3 stretch, which is assigned to a broad, featureless band at 2388 cm^{-1} in the infrared spectrum and a Raman band at 2392 cm^{-1}, is observed to shift on deuteration to 1788 cm^{-1}. The symmetric BH_3 stretch is observed at 2352 cm^{-1} in the "light" molecule and the symmetric BD_3 stretch at 1700 cm^{-1} in the deuterated species.

The symmetric BH_3 deformation is the only boron–hydrogen motion to exhibit a resolvable ^{10}B–^{11}B isotopic shift in the "light" compound. The symmetric $^{10}BH_3$ and $^{11}BH_3$ deformations are observed at 1065 and 1056 cm^{-1}, respectively. The antisymmetric BH_3 deformation is observed at 1137 cm^{-1}. The symmetric $^{11}BH_3$ deformations, being the most intense band in the infrared spectrum, would be

[11] G. Bouquet and M. Bigorgne, *Spectrochim. Acta, Part A*, **23**, 1231 (1967).

Table III. Fundamental Frequencies and Assignments for $(CH_3)_3As{\cdot}BH_3$[a]

$(CH_3)_3As{\cdot}BH_3$		$(CH_3)_3As$[b]		$(CH_3)_3As{\cdot}BH_3$	
Infrared ν, cm^{-1}	Raman $\Delta\nu$, cm^{-1}	Infrared ν, cm^{-1}	Raman $\Delta\nu$, cm^{-1}	Calcd freq, cm^{-1}	Assignment and approx description
2997 w	2993 s	2990	2980	2995	$\nu_1(A_1)$, $\nu_{16}(E)$, $\nu_{17}(E)$ CH_3 antisym str (100%)
		2935			$\nu_2(A_1)$, $\nu_{18}(E)$ CH_3 sym str (100%)
2922 mw	2923 vs	2920	2906	2922	
		2906			
2388 vs	2392 s			2385	$\nu_{19}(E)$ BH_3 antisym str (100%)
2348 vs	2352 vs			2358	$\nu_3(A_1)$ BH_3 sym str (100%)
1430 m		1436		1425	$\nu_{20}(E)$ CH_3 antisym def (100%)
1422 m	1424 m	1427	1416	1425	$\nu_{21}(E)$
1414		1417		1424	$\nu_{24}(A_1)$
	1285 wm	1283		1276	$\nu_5(A_1)$ CH_3 sym def (100%)
1272 w	1270 w	1270	1263		
1265 mw		1260		1279	$\nu_{22}(E)$
1253 w	1257 wm	1252	1242		
1137 s	1143 m			1139	$\nu_{23}(E)$ BH_3 antisym def (100%)
1065 s				1068	$\nu_6(A_1)$ $^{10}BH_3$ sym def (100%)
1056 vs				1059	$\nu_6(A_1)$ $^{11}BH_3$ sym def (100%)
	923 w	896		925, 923	$\nu_7(A_1)$, $\nu_{24}(E)$ CH_3 rocks (100%)
912 vs	909 w	888	884	911	$\nu_{25}(E)$
		880			
855 s	856 w			846	$\nu_{26}(E)$ BH_3 rock (91%) and CH_3 antisym def (9%)
		591			
630 s	632 s	582	583	630	$\nu_{27}(E)$ AsC_3 antisym str (97%)
		570			
609 s	612 vs		568	610	$\nu_8(A_1)$ AsC_3 sym str (85%), As–B str (7%), and CH_3 sym def (5%)
512 w	515 wm			510	$\nu_9(A_1)$ As–^{10}B str (83%) and AsC_3 sym str (17%)
497 s	501 s			496	$\nu_9(A_1)$ As–^{11}B str (87%) and AsC_3 sym str (13%)
	232 m		239	232	$\nu_{10}(A_1)$ AsC_3 sym def (90%) and AsC_3 sym str (10%)
	217 sh, m		223	217	$\nu_{28}(E)$ AsC_3 antisym def (95%) and AsC_3 antisym str (5%)
166 s	171 wm			165	$\nu_{30}(E)$ BAsC bend (97%)

[a] Abbreviations used: v, very; w, weak; m, medium; s, strong; sh, shoulder. [b] The infrared gas and Raman liquid frequencies are taken from P. J. D. Park and P. J. Hendra, *Spectrochim. Acta, Part A*, **24**, 2081 (1968), and ref 15, respectively.

expected to be the most intense band in the spectrum of the deuterium compound; therefore, the symmetric $^{11}BD_3$ deformation is assigned to the 816-cm^{-1} band. The band at 838 cm^{-1} is one-fourth as intense as the 816-cm^{-1} band; thus, it is assigned to the symmetric $^{10}BD_3$ deformation. By using the Teller-Redlich product rule in conjunction with the other nine assigned A_1 modes, a minimum frequency for the symmetric BD_3 deformation was calculated which is consistent with this assignment. The remaining band at 830 cm^{-1} is assigned to the antisymmetric BD_3 deformation. The BH_3 rock is assigned to a strong infrared band at 855 cm^{-1} and is observed to shift to 630 cm^{-1} on deuteration.

The As-B stretch mixes less with the symmetric AsC_3 stretch than the other group Va analogs as expected on the basis of the arsenic atomic mass. The As-B stretch shows ^{10}B-^{11}B isotopic splitting. The As-^{10}B and As-^{11}B stretches are observed at 512 and 497 cm^{-1}, respectively, and shift upon deuteration to 468 and 458 cm^{-1}, respectively.

Normal-Coordinate Analysis

The normal-coordinate analysis was undertaken to aid in the assignment of the borane group modes and to determine how the force constants for the borane group compared with the force constants determined by previous normal-coordinate calculations of nitrogen- and phosphorus-boron adducts.[4,6] The analysis was made using the Wilson **GF** matrix method[12] and programs written by Schachtschneider.[13] The **G** matrix was calculated using the structural parameters determined from the microwave study. The frequencies were weighted by $(1/\lambda)$ in the least-squares routine. Initial force constants for the borane group were taken from published values reported by Odom, *et al.*[6] Typical values for the methyl group force constants were selected from the work of Duncan.[14] Values for the ∠CAsC bend and As-C stretch were taken from the published work of Bouquet and Bigorgne.[11] An initial force field of 27 force constants was employed to fit 54 frequencies. Since many of the frequencies for the normal modes of the isotopic molecules were the same as those for the corresponding motions in the "light" molecule, there were only 33 independent frequencies. Since the **J'WJ** matrix is important to the calculation of the least-squares fit, the determinant of the matrix was tested for singularity after each iteration and the magnitude compared to the trace of the matrix as described by Schachtschneider.[13] The calculated frequencies of $(CH_3)_3As{\cdot}BH_3$ and $(CH_3)_3As{\cdot}BD_3$ are listed in Tables III and IV with average errors of 0.3 and 0.4%, respectively. In the final calculation of the force field, only the 20 force constants (Table V) with magnitudes greater than 0.02 mdyn/Å were used. The following interaction force constants were included in some of the initial calculations but were found not to improve the fit appreciably: F_{RQ}, F_Q, $F_{R\beta}$, F_δ, $F_{\alpha\phi}$, and $F_{Q\beta}$. During the latter stages of the refinement, the ten principal force constants and the PED were invariant to changes in the interaction force constants.

Previously, two VFF normal-coordinate analyses have been

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(12) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra," McGraw-Hill, New York, N. Y., 1955.

(13) J. H. Schachtschneider, Technical Reports No. 231-64 and 57-65, Shell Development Co., Emeryville, Calif., 1964 and 1965.

(14) J. L. Duncan, *Spectrochim. Acta*, 20, 1197 (1964).

Table IV. Fundamental Frequencies and Assignments for $(CH_3)_3As{\cdot}BD_3$[a]

$(CH_3)_3AsBD_3$ Infrared ν, cm^{-1}	$(CH_3)_3AsBD_3$ Raman $\Delta\nu$, cm^{-1}	$(CH_3)_3As$[b] Infrared ν, cm^{-1}	$(CH_3)_3As$[b] Raman $\Delta\nu$, cm^{-1}	$(CH_3)_3AsBD_3$ Calcd freq, cm^{-1}	Assignment and approx description
2995	3004	2990	2980	2995	$\nu_1(A_1)$, $\nu_{16}(E)$, $\nu_{17}(E)$ CH_3 antisym str (100%)
2921	2924	2935	2906	2922	$\nu_2(A_1)$, $\nu_{18}(E)$ CH_3 sym str (100%)
		2920			
1806	1816	2906		1812	$\nu_{19}(E)$ $^{10}BD_3$ antisym str (100%)
1788	1800			1791	$\nu_{19}(E)$ $^{11}BD_3$ antisym str (100%)
1712	1719			1692	ν_3 (A_1) $^{10}BD_3$ sym str (100%)
1700	1709			1688	ν_3 (A_1) $^{11}BD_3$ sym str (100%)
1436	1437	1436		1425	$\nu_{20}(E)$
	1431	1427	1415	1424	$\nu_{21}(E)$ CH_3 antisym def (100%)
1418	1426	1417		1425	$\nu_4(A_1)$
	1284	1283		1276	$\nu_5(A_1)$
1274		1270	1263		CH_3 sym def (100%)
1265	1269	1260		1279	$\nu_{22}(E)$
1258	1253	1252	1242		
925	918	896		926, 922	$\nu_7(A_1)$, $\nu_{24}(E)$ CH_3 rocks (95%)
910		888	884	911	$\nu_{25}(E)$
		880			
838				833	$\nu_6(A_1)$ $^{10}BD_3$ sym def (90%) and As–B str (10%)
830	835			824	$\nu_{23}(E)$ BD_3 antisym def (100%)
816	818			819	$\nu_6(A_1)$ $^{11}BD_3$ sym def (90%) and As–B str (10%)
630	633			637	$\nu_{26}(E)$ BD_3 rock (85%) and AsC_3 antisym str (15%)
		591			
630	633	582	583	629	$\nu_{27}(E)$ AsC_3 antisym str (95%)
		570			
605	608		568	602	$\nu_8(A_1)$ AsC_3 sym str (85%) and CH_3 sym def (8%)
468	470			471	$\nu_9(A_1)$ As–^{10}B str (86%) and AsC_3 sym str (14%)
458	461			461	$\nu_9(A_1)$ As–^{11}B str (86%) and AsC_2 sym str (14%)
	232		239	232	$\nu_{10}(A_1)$ AsC_3 sym def (85%) and As–B str (10%)
	216		223	217	$\nu_{28}(E)$ AsC_3 antisym def (95%)
151	154			153	$\nu_{30}(E)$ BAsC bend (90%) and BD_3 antisym def (5%)

[a] For abbreviations used, see Table I. [b] The infrared gas and Raman liquid frequencies are taken from P. J. D. Park and P. J. Hendra, *Spectrachim. Acta, Part A,* **24**, 2081 (1968), and ref 15, respectively.

Table V. Internal Force Constants for $(CH_3)_3As$ and $(CH_3)_3As{\cdot}BH_3$

Force const	Group	Force const value,[a] mdyn/Å $(CH_3)_3As$	Force const value,[a] mdyn/Å $(CH_3)_3As{\cdot}BH_3$
K_R	As–B str		1.84 ± 0.02
K_Q	As–C str	2.56 ± 0.04	2.97 ± 0.02
K_r	B–H str		3.06 ± 0.01
K_q	C–H str	4.77 ± 0.01	4.82 ± 0.01
H_α	∠CAsC bend	0.99 ± 0.04	0.69 ± 0.02
H_β	∠CAsB bend		0.52 ± 0.02
H_γ	∠HBH bend		0.38 ± 0.01
H_δ	∠AsBH bend		0.58 ± 0.01
H_σ	∠HCH bend	0.53 ± 0.01	0.53 ± 0.01
H_ϕ	∠AsCH bend	0.51 ± 0.01	0.55 ± 0.01
$F_{R\delta}$	As–B str–∠AsBH bend		0.21 ± 0.01
$F_{Q\alpha}$	As–C str–∠CAsC bend	0.28 ± 0.04	−0.21 ± 0.04
$F_{Q\delta}$	As–C str–∠AsBH bend		0.09 ± 0.02
$F_{Q\phi}$	As–C str–∠AsCH bend	0.41 ± 0.02	0.43 ± 0.01
F_γ	B–H str–B–H str		0.08 ± 0.01
F_q	C–H str–C–H str	0.05 ± 0.01	0.03 ± 0.01
F_β	∠CAsB bend/∠CAsB bend		0.14 ± 0.02
$F_{\beta\delta}$	∠CAsB bend–∠AsBH bend		0.08 ± 0.02
$F_{\beta\phi}$	∠CAsB bend–∠AsCH bend		0.04 ± 0.01
F_ϕ	∠AsCH bend–∠AsCH bend		−0.05 ± 0.01
F_α	∠CAsC bend–∠CAsC bend	0.18 ± 0.03	

[a] The bending force constants are divided by 1 Å.

carried out for $(CH_3)_3As$.[11,15] In both of the analyses the methyl groups were treated as point masses of mass 15. A two force constant force field was used to calculate the AsC_3 stretch and AsC_3 deformation of A_1 symmetry by Rosenbaum, *et al.*[15] In this earlier work by Rosenbaum, *et al.*, the assignments of the A_1 and the E AsC_3 deformations were reversed. Later, Bouquet and Bigorgne[11] reinvestigated the Raman spectrum of $(CH_3)_3As$ and corrected the assignment of the skeletal deformations and recalculated the normal-coordinate analysis employing a four force constant VFF force field. Only vibrational data for $(CH_3)_3As$ have been reported.

Since the only normal-coordinate analyses that have been reported previously for the Lewis base were made with the methyl group taken as a point mass of 15, a full normal-coordinate analysis was undertaken for $(CH_3)_3As$. The observed and calculated frequencies of $(CH_3)_3As$ are listed in Table VI with an average error of 0.3%. The structural parameters used in the calculation of the G matrix were taken from the microwave work by Lide.[9] An initial force field of 13 force constants was employed. In the final calculation of the VFF force field, the nine force constants listed in Table V were used to calculate 17 frequencies. The interaction force constants, F_Q, F_σ, and F_ϕ, included in some of the initial calculations, were dropped because they were insignificant.

The principal trouble with a two force constant force field used by Rosenbaum, *et al.*,[15] initially for $(CH_3)_3As$ is the inability of such a force field to consider coupling between the normal modes. Bouquet and Bigorgne[11] improved upon the force field of Rosenbaum, *et al.*,[15] by considering a stretch-stretch interaction between the As–C bond stretches and a bend-bend interaction between the ∠CAsC bends. These authors tried to calculate a force field with a stretch-bend interaction instead of a bend-bend interaction; however, they were unable to obtain a solution. Both skeletal deformations couple with the AsC_3 stretch of their respective symmetries. In addition to the AsC_3 stretch-bend interaction and the AsC_3 bend-bend interaction, the neglect of the significant interaction constants AsC_3 stretch-bend and AsC_3 stretch-CH_3 rock resulted in a value of 0.80 mdyn/Å for the

(15) E. J. Rosenbaum, D. J. Rosenbaum, D. J. Rubin, and C. R. Sandberg, *J. Chem. Phys.*, 8, 366 (1940).

Table VI. Fundamental Frequencies and Assignments for $(CH_3)_3As^a$

Infrared ν, cm^{-1}	Raman $\Delta\nu$, cm^{-1}	Calcd freq, cm^{-1}	Assignment and approx description
2990	2980	2980	$\nu_1(A_1)$, $\nu_{12}(E)$, $\nu_{13}(E)$ CH_3 antisym str (100%)
2935			
2920	2906	2906	$\nu_2(A_1)$, $\nu_{14}(E)$ CH_3 sym str (100%)
2906			
1436		1414	$\nu_{15}(E)$
1427	1416	1413	$\nu_{16}(E)$ CH_3 antisym def (100%)
1417		1412	$\nu_3(A_1)$
1283			
1270	1263	1262	$\nu_4(A_1)$ CH_3 sym def (100%)
1260			
1252	1242	1264	$\nu_{17}(E)$
896		886	$\nu_5(A_1)$ CH_3 rock (92%)
888	884	880	$\nu_{18}(E)$ CH_3 rock (93%)
880		870	$\nu_{19}(E)$ CH_3 rock (95%)
591			
582	583	583	$\nu_{20}(E)$ AsC_3 antisym str (90%) and CH_3 rock (10%)
570			
	568	568	$\nu_6(A_1)$ AsC_3 sym str (90%) and CH_3 rock (8%)
	239	239	$\nu_7(A_1)$ AsC_3 sym def (75%) and AsC_3 sym str (20%)
	223	223	$\nu_{21}(E)$ AsC_3 antisym def (90%) and AsC_3 antisym str (10%)

[a] For abbreviations used, see Table III. The infrared gas and Raman liquid frequencies are taken from P. J. D. Park and P. J. Hendra, *Spectrochim. Acta, Part A,* **24**, 2081 (1968), and ref 15, respectively.

AsC_3 bending force constant, which is significantly smaller than our value of 0.99 mdyn/Å. In both the calculations by Bouquet and Bigorgne[11] and this work the value of 2.56 mdyn/Å for the AsC_3 stretching force constant was obtained.

On formation of the adduct the AsC bond length decreased and the ∠CAsC bond angle increased. The AsC_3 stretching force constant increased from 2.56 mdyn/Å in the Lewis base to 2.97 mdyn/Å in the adduct. The PC_3 stretching force constant was observed to increase from 2.78 mdyn/Å in trimethylphosphine to 3.65 mdyn/Å in trimethylphosphine-borane. The increase in the AsC_3 stretching force constant in the adduct can be accounted for by the rehybridization of the Lewis base with compound formation.

Discussion

The Teller-Redlich product rule was calculated for the three isotopic species $(CH_3)_3As\cdot{}^{10}BH_3$, $(CH_3)_3As\cdot{}^{11}BD_3$, and $(CH_3)_3As\cdot{}^{10}BD_3$ for the A_1 and the E symmetry species. The errors in the product rule were 2.5 and 0.5% for the A_1 and E symmetry species, respectively.

The only mode in the trimethylarsine moiety of the adduct to show an isotopic shift on deuteration of the borane group was the symmetric AsC_3 stretching mode. Since the symmetric AsC stretch is mixed with the As-B stretch, the symmetric AsC_3 stretching mode would be expected to shift. The amount of mixing of the normal modes in the $(CH_3)_3M\cdot BH_3$ (M = N, P, As) adducts varies inversely with the mass of the M atom. The amount to which the symmetric MC_3 stretch is mixed with the MB stretch is 25, 25, and 13% in the $(CH_3)_3N\cdot BH_3$, $(CH_3)_3P\cdot BH_3$, and $(CH_3)_3As\cdot BH_3$ molecules, respectively. The AsC_3 stretching and ∠CAsC bending force constants were the only force constants to change appreciably with adduct formation and all the changes in the force constants of trimethylarsine are attributed to the increase of s character in the rehybridization around the arsenic atom.

The AsC_3 deformations were not observed in the infrared spectrum of trimethylarsine-borane. The order of intensity of the MC_3 deformations in the infrared spectrum is observed to be $(CH_3)_3N\cdot BH_3 > (CH_3)_3P\cdot BH_3 > (CH_3)_3As\cdot BH_3$. Indeed, these skeletal deformations were not observed in the infrared spectrum of $(CH_3)_3As\cdot BH_3$. The skeletal deformations were observed to be medium or strong bands in the Raman spectra of all three adducts.

None of the torsional modes were observed for trimethylarsine-borane. The BH_3 torsion and the methyl in-phase torsion are of A_2 symmetry and none of the five "silent" A_2 modes were observed. The out-of-plane methyl torsion was the only unobserved E mode. The fact that none of the E modes were split nor none of the A_2 modes observed is consistent with C_{3v} site symmetry.

Trimethylarsine-borane, like trimethylamine-borane and trimethylphosphine-borane, satisfies Timmermans' criteria[16] for a globular molecule. Molecules of this type often form plastic crystals in which the effects of site symmetry should be very small. Neither site nor factor group splittings were observed in the present study. Neither were any lattice modes observed in the Raman spectrum which is in marked contrast to the spectrum of trimethylphosphine-borane but similar to that of trimethylamine-borane. The failure to observe lattice modes in either spectrum is consistent with one molecule per primitive cell or it may simply reflect the fact that they are too weak to be observed.

In a comparison of some of the structural parameters of the Lewis base and the borane adduct, the As-C bond distance is more than 0.01 Å shorter in the adduct. Also, the ∠CAsC angle has increased by approximately 9° in the adduct. Both of these changes are consistent with a rehybridization around the arsenic atom to a larger percentage of sp^3 bonding character. These changes are analogous to those found in the corresponding trimethylphosphine adduct[10] but are in contrast to the longer N-C distance and smaller ∠CNC angle found in the corresponding trimethylamine adduct.[5] The changes in the trimethylamine structural parameters result from electron withdrawal rather than rehybridization with adduct formation. The As-B distance of 2.035 Å compares favorably with the value of 2.02 Å predicted[17] from the sum of the covalent radii of these two atoms. There do not appear to have been any other boron-arsenic bond distances measured to compare with this value. As expected, the stability of the trimethylarsine-borane molecule is less that that of the corresponding amine and phosphine adducts. This trend is reflected in the values of the M-B stretching force constants: N-B, 2.59 mdyn/Å; P-B, 2.37 mdyn/Å;

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(16) J. Timmermans, *J. Phys. Chem. Solids,* 18, 1 (1961).

(17) L. Pauling, "Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960.

As-B, 1.84 mdyn/Å. There appear to have been no other As-B force constants previously reported with which we can compare our value.

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Synthesis of *nido*- and *closo*-Arsacarboranes

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Reaction of $Tl_27,8$-$C_2B_9H_{11}$ with $RAsX_2$ (R = CH_3, X = Br; R = C_6H_5, n-C_4H_9, X = Cl) in diethyl ether solution produced compounds characterized as 3-R-3-As-1,2-$C_2B_9H_{11}$. Spectral data indicate closo icosahedral structures for these species. Reaction of 3-C_6H_5-3-As-1,2-$C_2B_9H_{11}$ with BBr_3 afforded 3-Br-3-As-1,2-$C_2B_9H_{11}$. Reaction of $(CH_3)_2AsBr$ with $Tl_2C_2B_9H_{11}$ in a 2:1 ratio afforded $[(CH_3)_2As]_2C_2B_9H_{11}$. Spectral and chemical data suggest a nido 12-vertex structure for this species with one $(CH_3)_2As$ group terminally bonded to boron.

Introduction

Base degradation of 1,2-$C_2B_{10}H_{12}$ yields the dodecahydro-7,8-dicarba-*nido*-undecaborate(1−) ion[1] which may be subsequently converted to the undecahydro-7,8-dicarba-*nido*-undecaborate(2−) ion, 7,8-$C_2B_9H_{11}^{2-}$.[2] The structure of 7,8-$C_2B_9H_{11}^{2-}$ is that of a nearly regular icosahedron with one vertex missing.[3] A number of reactions of this dianion with various reagents which result in reconstruction of the closed polyhedron have been established over the past few years.[4] However, no such reactions involving group V reagents have been reported, although Todd and coworkers have formally substituted a group V atom for a carbon atom in carborane, obtaining a heteroborane containing ten boron atoms as well as one carbon atom and one arsenic or phosphorus atom.[5]

Our attempts to prepare group V atom heterocarboranes analogous to the $RAlC_2B_9H_{11}$ and $RBC_2B_9H_{11}$ systems, previously prepared and reported by workers from this laboratory,[6,7] have led to the synthesis of two new types of heteroboranes derived from 7,8-$C_2B_9H_{11}^{2-}$ and organoarsenic halides. We report herein the synthesis and characterization of $RAsC_2B_9H_{11}$ (R = CH_3, n-C_4H_9, C_6H_5, and Br) and $[R_2As]_2C_2B_9H_{11}$ (R = CH_3) species.

Results and Discussion

Synthesis and Characterization of 3-Substituted 3-Arsa-1,2-dicarba-*closo*-dodecaboranes. The general approach to the preparation of group III derivatives of 7,8-$C_2B_9H_{11}^{2-}$ involves proton abstraction from the 7,8-$C_2B_9H_{12}^-$ ion with sodium hydride in tetrahydrofuran (THF) or benzene followed by the addition of the appropriate group III reagent,[6,7] $RAlX_2$ or RBX_2.

$$7,8\text{-}C_2B_9H_{12}^- + NaH \xrightarrow{THF} Na^+\text{-}7,8\text{-}C_2B_9H_{11}^{2-} + H_2 \quad (1)$$

$$Na^+\text{-}7,8\text{-}C_2B_9H_{11}^{2-} + RAlX_2 \xrightarrow{THF} RAlC_2B_9H_{11} + 2X^- \quad (2)$$

Our first attempts to duplicate this sequence for the preparation of arsacarboranes resulted in the formation of yellow solids which we have thus far been unable to characterize. When proton abstraction from the 7,8-$C_2B_9H_{12}^-$ species was carried out by allowing the trimethylammonium salt of 7,8-$C_2B_9H_{12}^-$ to react with n-butyllithium in diethyl ether[8] and the resulting solution treated with dibromomethylarsine, a very low yield of a yellow compound identified by mass spectral analysis as the desired $CH_3AsC_2B_9H_{11}$ species was isolated. The yellow gums, which constituted the major reaction product, appeared to be low molecular weight polymers.

$$[(CH_3)_3NH][7,8\text{-}C_2B_9H_{12}] + 2n\text{-}C_4H_9Li \xrightarrow{(C_2H_5)_2O} Li_2[7,8\text{-}C_2B_9H_{11}] + (CH_3)_3N + 2n\text{-}C_4H_{10} \quad (3)$$

$$Li_2[7,8\text{-}C_2B_9H_{11}] + CH_3AsBr_2 \xrightarrow[0°]{(C_2H_5)_2O} CH_3AsC_2B_9H_{11} + \text{yellow polymer} + 2LiBr \quad (4)$$

When the reactions, represented by eq 3 and 4, were carried out in benzene, hexane, toluene, THF, or glyme solutions, none of the desired product was obtained.

During the course of our studies, Spencer, Green, and Stone reported the synthesis of a thallium salt of 7,8-$C_2B_9H_{11}^{2-}$, $Tl_2C_2B_9H_{11}$, which they found to be air and water stable (unlike the alkali metal salts) allowing easy storage and handling.[9] Reaction of $Tl_2C_2B_9H_{11}$ with organodihaloarsines gave the desired 3-alkyl- or 3-aryl-3-arsa-

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