fluoride and carbon dioxide were formed, whereas in a platinum vessel arsenic trifluoride and a polymer (polytetrafluoroethylene) were observed. We feel that this is good evidence for primary formation of CF_2 as well as CF_3 radicals in the decomposition of tris(trifluoromethyl)arsine. Further pyrolysis studies in the absence of glass, which probably reacts with arsenic trifluoride to give silicon tetrafluoride, would be of interest in view of the similar breakdown pattern observed in the mass spectrometer.

Experimental Section

The compounds were prepared by the literature methods[9-11] and their purity established by molecular weight determinations and infrared spectroscopy. Mass spectra were recorded on an A.E.I. MS9 operating at 70 ev, samples being introduced as vapor through a heated inlet at 185°. Perfluorotributylamine was added in some cases to assist in the counting of the spectrum.

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The Vibrational Spectrum of Borazine[1a]

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The vibrational spectrum of borazine, $(-BH-NH-)_3$, has been reexamined using isotopically labeled derivatives. On the basis of this study a revised assignment for a number of frequencies of the borazine spectrum is suggested. In particular, the two BN ring vibrations of species E′ have been identified at 1465 and 1406 cm^{-1} (gas phase spectrum), respectively.

Introduction

Borazine, $(-BH-NH-)_3$, the "inorganic benzene," has been known for more than 30 years, and its Raman and infrared spectrum was studied as early as 1939.[2] The basic assignments of the fundamental vibrations as suggested by Crawford and Edsall[2b] were refined by some later work[3] and have since been commonly accepted. Certain discrepancies between the observed and calculated values for out-of-plane hydrogen vibrations of the molecule were reinvestigated by Spurr and Chang,[4] and the assignments of BH and NH deformational modes of borazine are still somewhat controversial.[5] On the basis of their data Kubo and his coworkers[5] suggested that BH bending modes should occur at higher frequencies than the corresponding NH vibrations in each species. Nevertheless, the original assignments of the vibrational modes of borazine have generally been used in analyzing the spectra of substituted borazines. Only Becher[6] questioned the assignments of the B–N ring modes of species E′ of borazine, but no attempt was made to clarify that situation.

Recent studies of the vibrational spectra of other boron–nitrogen heterocycles containing the N–B–N entity raised some doubt about the validity of the original assignments for certain vibrational modes of borazine and have prompted a reexamination of the molecule. The findings of this study are substantiated through observations of isotopically labeled derivatives. The data resulting from isotope studies clarify several features of the vibrational spectrum of borazine which previously could not be resolved.

Due to multiple possibilities for labeling the borazine molecule, this compound is particularly suitable for a detailed study of isotope effects and a subsequent mathematical treatment. The results of such work based on the present experimental data will be reported elsewhere.

The authors gratefully acknowledge access to an unpublished manuscript on the vibrational spectra of B-trihaloborazines due to the courtesy of Professor J. Goubeau, Technische Hochschule Stuttgart, Germany.[7] This work arrives at conclusions similar to those arising from the present study with respect to the reassignment of the vibrational spectrum of borazine.

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[1] (a) Supported in part by the U. S. Army Research Office, Durham, N. C.; (b) Duke University; (c) Visiting Lecturer at Duke University from the Laboratorium für anorganische Chemie, Technische Hochschule Stuttgart, Germany; (d) Shionogi Research Laboratory.

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Experimental Section

($-{}^{10}BH-NH-)_3$.—Boron-10 enriched B-trichloroborazine was prepared from boric acid containing 92% ^{10}B, obtained from the Oak Ridge National Laboratory. The acid was converted to $^{10}BCl_3$ by a method developed by Becher.[8] A modified[9] Brown–Laubengayer synthesis[10] effected by allowing the $^{10}BCl_3$ to react with ammonium chloride in chlorobenzene gave the desired ($-{}^{10}BCl-NH-)_3$. The boron-10 enriched B-trichloroborazine was reduced to ($-{}^{10}BH-NH-)_3$ by a standard procedure[11] using sodium hydroborate in diglyme solution.

($-BH-ND-)_3$.—This compound was prepared by a previously reported method.[5]

($-BD-NH-)_3$.—B-Trideuterioborazine was obtained by the standard reduction[11] of commercially available B-trichloroborazine with sodium deuterioborate.[12]

($-BD-ND-)_3$.—Hexadeuterioborazine was obtained by reducing B-trichloro-N-trideuterioborazine[5] with sodium deuterioborate.

Deuterated boron-10 labeled borazines were prepared by analogous procedures as cited above but using ($-{}^{10}BCl-NH-)_3$ as starting material.

Recording of Spectra.—Infrared spectra in the 250–4000 cm^{-1} region of the various isotopically labeled borazines were recorded from the gas phase with a Beckman IR-12 instrument. A cell of 10-cm path length equipped with KRS-5 windows was used, and spectra were recorded at various pressures at room temperature. For high-resolution work, the slit width of the instrument was reduced to $^1/_2$ and $^1/_3$, respectively of the standard slit program. Also, some spectra were recorded on liquid capillary films. All Raman spectra were obtained from the pure liquids with a Cary Model 81 Raman spectrometer using Raman cuvettes of 7-mm diameter; Polaroid foil was used for polarization measurements. In all cases the frequency values listed are the averages of several recordings.

The Vibrational Spectrum of Borazine

Borazine, ($-BH-NH-)_3$, consists of a planar ring structure of alternating BH and NH groups.[13] Therefore, the heterocycle has D_{3h} symmetry; the expected fundamental vibrations of the molecule are listed in Table I.

In addition to the selection rules, information for an assignment of the normal vibrations can be obtained by studying the infrared band contours of the gaseous compounds.[14] Borazine is an oblate symmetric top molecule with $I_A = 2I_B = 2I_C$. Therefore, for vibrations of species A_2'', one expects a PQR structure with a prominent Q branch. On the basis of the borazine structure[13] it is possible to calculate the separation $\Delta\nu_{PR}$ of parallel bands between the maxima of the P and R branch envelopes.[15] For ($-BH-NH-)_3$, $\Delta\nu_{PR}$ should be 24.2 cm^{-1} with only slight variations by the isotopically labeled derivatives (see Table II).

For the perpendicular bands of species E′, however, the band contours depend strongly on the Coriolis coupling coefficients ζ, which may be different for each normal vibration of this species. The perpendicular band envelopes have been calculated for symmetric top molecules[16] and the resultant data were used to evaluate the expected $\Delta\nu_{PR}$ for different ζ values. These results including a description of the band envelopes are illustrated in Table II. For a given ζ value, isotopic substitution has only a minor influence but it should be noted that, for a particular normal vibration, the ζ coefficient *per se* may vary with isotopic substitution. Therefore, the band shape of the same vibration of species E′ may be different for various isotopically labeled borazines. For $\zeta \approx -0.60$, the spacing and band shape of an E′ band is almost identical with that of A_2'' bands.

TABLE I

THE FUNDAMENTAL VIBRATIONS OF BORAZINE[a]

Species	Number and activity (Raman; infrared)	Properties	Modes
A_1'	4 (p; ia)	In-plane	ν_1 ν_sNH
		In-phase	ν_2 ν_sBH
			ν_3 ν_sBN(ring)
			ν_4 δ_sBN(ring)
A_2'	3 (ia; ia)	In-plane	ν_5 $\nu_{as}BN$(ring)
		In-phase	ν_6 δBH
			ν_7 δNH
A_2''	3 (ia; a)	Out-of-plane	ν_8 γBH
		In-phase	ν_9 γNH
			ν_{10} γBN(ring)
E′	7 (dp; a)	In-plane	ν_{11} $\nu_{as}NH$
		Out-of-phase	ν_{12} $\nu_{as}BH$
			ν_{13} $\nu_{as}BN$(ring)
			ν_{14} $\nu_{as}BN$(ring)
			ν_{15} δBH
			ν_{16} δNH
			ν_{17} δBN(ring)
E″	3 (dp; ia)	Out-of-plane	ν_{13} γBH
		Out-of-phase	ν_{19} γNH
			ν_{20} γBN(ring)

[a] p, polarized; dp, depolarized; a, active; ia, inactive.

The element boron exists as two stable isotopes, ^{11}B and ^{10}B, with a natural abundance of about 4:1. Since three boron atoms are incorporated into a borazine molecule, one expects a concentration of each isotope as follows. The per cent of natural abundant boron as opposed to the per cent of boron-10 enriched boron (92% ^{10}B) is for $^{11}B^{11}B^{11}B$, 51 *vs.* 0.05; $^{11}B^{11}B$-^{10}B, 38 *vs.* 1.8; $^{11}B^{10}B^{10}B$, 10 *vs.* 20; $^{10}B^{10}B^{10}B$, 1 *vs.* 78. Therefore, each vibration associated with a boron atom should exhibit band splitting into at least two peaks. Certainly this effect will not always be seen; however, it should be clearly evident for most BN ring modes. This event is apparent from the data in Table III, listing the Raman and infrared spectrum of ($-BH-NH-)_3$ and ($-{}^{10}BH-NH-)_3$. Spectra of isotopically labeled borazines are listed in Tables III–VI.

The intensities of the infrared bands observed near 1174 and 1603 cm^{-1}, respectively, in the spectra of ($-BH-NH-)_3$ and ($-BH-ND-)_3$ and their boron-10 enriched derivatives increase with the age of the borazine sample. It is known that, under these circum-

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TABLE II

SHAPE AND $\Delta\nu_{PR}$ OF THE A_2'' AND E' BANDS OF BORAZINE

Species	ζ	Band shape	$\Delta\nu_{PR}$, cm^{-1}		
			$(-^{10}BH-NH-)_3$	$(-BH-NH-)_3$	$(-BD-NH-)_3$
A_2''			24.5	24.2	22.0
E'	1.00	One line without structure	0	0	0
	0.75	PR structure (no observable Q branch) with increased merging of the band maxima	6.3	6.2	5.7
	0.50		10.4	10.3	9.4
	0.25	↓	13.6	13.4	12.2
	0.00	PQR branches of about equal intensity	16.7	16.4	15.0
	−0.25	PQR structure with increased prominence of Q branch	20.9	20.6	18.8
	−0.50		24.0	23.7	21.6
	−0.75		26.1	25.8	23.5
	−1.00	↓	27.9	27.5	25.1

TABLE III

THE VIBRATIONAL SPECTRUM OF $(-BH-NH-)_3$ AND $(-^{10}BH-NH-)_3$[a]

$(-BH-NH-)_3$			$(-^{10}BH-NH-)_3$		
Raman	Infrared (gas)		Raman	Infrared (gas)	
288 wm, dp			291 m, dp		
	380/394/407	s (PQR)		383/391; 394; *396.5*/409	s (PQR)
521 wm, dp	506/518/532	w (PQR)	527 mw, dp	514/*526*; 527.5/539	w (PQR)
	651/658	vw (PR)		661/667	vw (PQR)
	706/715; *719*; 721/723/732	s (PQR)		713/721; 723; 724.5; *725.5*/739	s (PQR)
798 vw	780/790/803	wm (PQR)		779/789/809	wm (PQR)
852 s, p	798	w	852 s, p	798/803.5	w
	905/915; *917.5*/932	vs (PQR)			
	927	s (Q, B-10)		917/930/944	vs (PQR)
940 vs, p			948 w, sh		
953 sh, p			978 vs, p		
968 w	972/975	vw[b]			
	994	w		998/1005/1013	w (PQR)
	1014	sh			
1070 m, dp	1090/1096/1107	wm (PQR)	1073 m, dp	1094/1102/1111	wm (PQR)
	1155/1171; *1173*; 1175/1195	wm[b] (PQR)		1160/1181/1203	w (PQR)[b]
				1216	vw
	1299/1305/1313	w (PQR)		1314/1321/1331	wm (PQR)
	1365	vw		1366/1376/?	m (PQR)
	1380	vw			
1371 w (b), dp	1399/1406/1412	m (PQR)	1392 w, dp	1401/1408/1416	m (PQR)
1458 w, dp	1456/1465/1474	vs (PQR)	1475 w, dp	1483/1492	vs (PR)
	1587/1603/1624	m[b] (PQR)		1589/1607.5/1626	m (PQR)[b]
	1730/1741/1760	vw (PQR)		1760/1773/1785	vw (PQR)
	1820	vw			
	1833	w		1858	w
	1863	wm		1845/1886/1917	wm (PQR)
	1918	w			
	2006	w		2004/2012	w (PR)
	2148/2159	wm		2177/2190/2201	m (PQR)
				2232	vw (Q)
	2228	vw (Q)			
	2318	vw		2352/2365	w
	2400/2408	m	2425 vw	2410/2423	m
			2490 wm, p	2501/2508	s
2510 w (sh), dp	2514/2520/2527	vs (PQR)	2532 sh	2518/2535/2545	vs
2535 vs, p			2554 s, p		
	2589/2598	w[b]		2632/2643/2652	m (PQR)
	2670	vw		2724	sh
				2813	vw
	2833	w		2871	w
	2939	w		2950/2976/2975	wm (PQR)
3453 vs, p			3452 vs, p		
	3477	s (PQR)		3478/3486/3493	s (PQR)

[a] w, weak; m, medium; s, strong; v, very; sh, shoulder; p, polarized; dp, depolarized. [b] Impurity band (diborane).

stances, borazine decomposes with the formation of diborane (along with other products). Under high resolution it is possible to resolve some of the rotational lines of the P branch of the 1174 and 1603 cm^{-1} bands. These observations suggest that the two cited absorptions do not belong to borazine but rather indicate contamination of the samples with diborane. This assumption is supported by the fact that the two bands are identical in appearance and location with the two strongest bands observed in the spectrum of diborane.[17,18] The additional strong bands of diborane occurring in the 2525–2625 cm^{-1} region probably are obscured by absorptions of the borazine molecule. A minor contamination of the $(-BD-NH-)_3$ sample with diborane-d_6 is indicated by the observation of a very weak band at 1207 cm^{-1}. Identification of the

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Table IV

Vibrational Spectrum of B-Trideuterioborazine

(-BD-NH-)$_3$			(-^{10}BD-NH-)$_3$[a]	
Raman	Infrared (gas)		Infrared (gas)	
262 w, dp				
	314/324; *326.5*/339	ms (PQR)	313/326/338	ms (PQR)
	339/352/364	m (PQR)[b]	354	vw (Q)[b]
	374	vw		
509 wm, dp	499/509/518	w (PQR)	504/516/527	w (PQR)
			580	vw
			633	vw
	704/713; *716/728*	s (PQR)	*708*/719; 720; 721.5; *723/733*	s (PQR)
725 ms, dp				
			769/778	vw
788 vw	782/786	vw		
	797/804/808	vs/s/vs	805/807/809.5	w/w/m
	813/817/823	s/w/s/(R)	808/816; *819.5*/832	vs (PQR)
852 s, p				
903 vs, p				
920 sh?				
	903/*914.5*; 927/927; 972 sh	s (PQR)[b]	913/913; *927.5*/940	m (PQR)
1021 w, dp	1014/1022/1030	w (PQR)	1030	vw
1063 vw?	1053/1060	vw (PQR)		
	1094/1109	w	1109/1126	w
	1195/1207/1222	vw[c]	1208	vw[c]
			1249	vw
	1280	vw		
1328 w, dp	1323/1333	ms (PR)	1348/1362	vw
1345 sh				
	1390	m	1386/1397	m (PR)
1432 w, dp	1432/1440/1447	vs (PQR)		
1450 sh			1462	vs
	1551/1562; 1578/ 1590	wm (PQR)	1578	wm (Q)
			1600/1617	vw/w
			1653	vw (Q)
	1712/1727/1744	w (PQR)	1748	w (Q)
	1829	vw		
			1857/1865	wm
1893 s, p				
1920 sh	1892/1897/1906	vs (PQR)	1913/1921/1928	vs (PQR)
			1964	vw
	1988	vw		
	2000	vw		
	2045/2055	wm	2072/2080	w
	2130/2148/2163	w (PQR)	2167	vw (Q)
	2228	wm	2248	vw
	2290	m	2295	wm (Q)
	2412	wm		
	2542/2554	ms[b]	2545/2554	m[b]
	2708	w	2725	vw[b]
	2770	sh		
	2797	w	2805	vw
	2890	w	2842	vw
			2919	vw
	3240	vw	3270	vw
	3345	w	3380	vw
3452 vs, p				
	3479/3485/3493.5	s (PQR)	3477/3484/3492	s (PQR)
	3750	w		
	3997	w		

[a] Due to the small amount of material available no Raman spectrum could be recorded. [b] Impurity band due to presence of B–H. [c] Impurity band due to B_2D_6.

1174 and 1603 cm^{-1} absorptions of borazine as impurity bands is of major significance; both bands have previously[2b,3] been assigned to normal vibrations of the (-BH-NH-)$_3$ molecule.

The B-trideuterioborazine used in the present study contained some boron-bonded hydrogen, as evidenced by the infrared bands observed in the spectrum of (-BD-NH-)$_3$ near 2550 and 920 cm^{-1}. Only a very small amount of diborane-d_6 was present (very weak absorption at 1207 cm^{-1}), but no trace of B_2D_6 was detected in the spectrum of the perdeuterated borazine. All impurity bands are identified as such in Tables III–VI.

The assignments proposed for the vibrational frequencies of (-BH-NH-)$_3$ are based on the following considerations.

Species A$_1$'.—The assignment of the four totally symmetric vibrations of borazine has no inherent uncertainties. There are only four intense polarized Raman lines observed in the spectrum of borazine, all of which have been correctly assigned by Crawford and Edsall.[2b] The frequency of ν_1 decreases from 3453 cm^{-1} in (-BH-NH-)$_3$ to 2579 cm^{-1} [(-BH-ND-)$_3$] and 2567 cm^{-1} [(-BD-ND-)$_3$], respectively. The effect of deuteration at the boron atom on ν_2 is clearly seen. In borazine, this vibration is observed at 2535 cm^{-1}; upon B-deuteration it shifts to 1894 cm^{-1}. Replacing the natural boron by a ^{10}B enriched species causes a shift

TABLE V

VIBRATIONAL SPECTRUM OF N-TRIDEUTERIOBORAZINE

	(-BH-ND-)$_3$			(-^{10}BH-ND-)$_3$[a]	
	Raman	Infrared (gas)		Infrared (gas)	
	279 dp, m				
	397 w	367; *371*/383.5/397	s (PQR)	372/385/398.5	s (PQR)
	507 dp, wm				
	550 sh	536/*546*; 547; 548; 550/*561*	s (PQR)	539/*551*; 553.5/565	s (PQR)
	725 vw	695/*710*; 711.5/725	vw (PQR)	700/710.5/*712*; 714/726	vw (PQR)
	768 vw	768	m		
	796 w, dp	780/786/794	m (PQR)	786/796/805	m (PQR)
	824 s, p				
		889/*900*; 902; 904/914	vs (PQR)	902/*904*	w (Q?)
				901/910; *913.5*/927	vs (PQR)
		918/921	w	918	w (Q?)
	940 vs, p				
	951 m, p				
	965 wm, dp			1024	vw
				1037	vw
				1066	w, sh
	1051 vw?	1066/1071/1076	m (PQR)	1075	m
	1133 vw?				
		1177/1188	w[b]	1160/1181/1198	wm (PQR)[b]
	1283 vw (b)	1283/1289/1294	ms (PQR)	1293/1304/1320	ms (PQR)
		?/1332/1344	w (PQR)	1344/1356	vw
		1371	vw	1371	vw
	1422 w, dp	1429/1438/1449	vs (PQR)		
	1445 sh			1467/1477	vs (PR)[b]
		1587/1603/1620	wm (PQR)[b]	1590/1610/1630	m (PQR)[b]
		1761	vw	1774	w
	1795 w (b)			1798	vw
		1818	w (PQR)	1834	w
				1844	wm
		1895/1901/1908	m (PQR)	1920	w (Q)
		1925	sh	1955	vw
		2025	vw		
	2100 vw?			2060	wm
		2145	vvw	2168	w
		2185/2195	vw	2235	wm (Q)
	2267 vw	2258	vw		
		2294	vw	2297	vw
	2410 vw, dp	2408/2416.5/2426.5	m (PQR)	2427/2438/2445	m (PQR)
	2461 w, p				
2447 w, p	2492 sh, dp				
	2521 vs, p	2513/2519/2525	vs (PQR)	2515/2522/2530	vs (PQR)
	2548 wm				
	2579 vs, p			2593	w
		2588/2600	ms (PR?)	2615/2627	ms (PR?)
				2728	wm
		2790	vw	2802	w (Q)
	2825 vw	2870	w (b)		
		2900	sh		
				2945	m (Q)
		3100	vw (b)	3107	vw
				3410	vw
	3453 vw[c]	3480	w	3501	w
		3530	vw	3570	vw
				3612	vw
				3683	vw
				3681	vw

[a] Due to the small amount of material available no Raman spectrum could be recorded. [b] Impurity band due to diborane. [c] Impurity band due to (-BH-NH-)$_3$.

of ν_2 to 2554 cm^{-1}. The fact that ν_3 involves relatively large motions of the BH groups is evident from the frequency transitions from 940 to 978 cm^{-1} (^{11}B *vs.* ^{10}B) and from 940 to 903 cm^{-1} (BH *vs.* BD). The lowest band of species A_1', ν_4, is insensitive toward labeling at the boron sites of the molecule, but replacing the nitrogen-bonded hydrogen by deuterium decreases the frequency of ν_4 from 852 to 827 cm^{-1} (see Table VII).

The cited isotopic shifts of ν_3 and ν_4 seem to indicate that, in contrast to the results obtained from a consideration of the symmetry coordinates, these two modes may be viewed as vibrations of mixed stretching and deformational character. Primarily, one of the modes, ν_3, involves motions of the boron atoms, the other one those of the nitrogen atoms. These findings are in agreement with data reported by Hester and Scaife[19] in their study of the Raman spectra of B-trihaloborazines.

Species A_2''.—Crawford and Edsall[2b] suggested the following assignments for the three vibrations of species A_2'': $\nu_8 = 1088$ cm^{-1}, $\nu_9 = 649$ cm^{-1}, $\nu_{10} = 415$ cm^{-1}. Vibrational bands of species A_2'' (active only in the infrared) should exhibit a PQR structure with a prominent Q branch; in the case of (-BH-NH-)$_3$, a separation of $\Delta\nu_{PR} = 24.2$ cm^{-1} should be expected. In the spectrum of borazine, three bands showing these features are observed in accordance with the selection rules at 394, 719, and 917.5 cm^{-1}, respectively. In the spectra of the isotopically labeled borazines three ab-

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(19) R. E. Hester and C. W. J. Scaife, *Spectrochim. Acta*, **22**, 455 (1966).

TABLE VI

VIBRATIONAL SPECTRUM OF (–BD–ND–)$_3$[a]

Raman	Infrared (gas)		Raman	Infrared (gas)	
255 s					
	310/323/333	m (PQR)	1220 w		
	467	vw		1245	vw
499 mw	487	w		1322	w
	527/538.5; *540*/551	s (PQR)		1333	sh
				1410	sh
	625	vw	1410 vw?	1418	vs
723 m	725	w		1445	sh
	766.5; 775	wm		1530	w
	770/782.5/795	s (PQR)	1895 ms	1888/1895/1902	vs (PQR)
	788	vw		1940	vw
	792	s		2042	vw
	797	m		2150	vw
	801	vw		2253	vw
824 s				2465	vw
	880	vw		2540	w[b]
901 vs			2567 vs		
	906	wm (Q)[b]		2582	ms
	921	vw		2635	w
1055 vw?				3485	vw
	1070	w (b)			

[a] Due to the small amount of material available no polarization measurements could be made. [b] Impurity band due to (–BH–NH–)$_3$.

sorptions are observed which correspond in shape and intensity with the cited modes and also show the expected isotopic shifts, thus lending credence to the revised assignments.

The γNH character of the borazine band observed at 719 cm^{-1} is apparent from the considerable effect of N-deuteration and the relative consistency in band position by deuteration at the boron atoms (see Table VII). This same mode is also observed at 706 cm^{-1} in the spectrum of B-trichloroborazine, by a shift to 503 cm^{-1} in (–BCl–ND–)$_3$.[5] The 394 cm^{-1} absorption shifts only to a minor degree by isotopically labeling the borazine molecule; it is readily assigned to the ring mode ν_{10}.

TABLE VII

ISOTOPIC SHIFTS OF THE BORAZINE FUNDAMENTALS[a]

Normal vibrations		(–BD–ND–)$_3$	(–BD–NH–)$_3$	(–^{10}BD–NH–)$_3$	(–BH–NH–)$_3$	(–^{10}BH–NH–)$_3$	(–BH–ND–)$_3$	(–^{10}BH–ND–)$_3$	(–BD–ND–)$_3$
A$_1$′	ν_1	2567	3452	. . .	3452	3452	2579	. . .	2567
	ν_2	1895	1893	. . .	2535	2554	2521	. . .	1895
	ν_3	901	903	. . .	940	978	940	. . .	901
	ν_4	824	852	. . .	852	852	824	. . .	824
A$_2$″	ν_8	782.5	808	819.5	917.5	930	900	913.5	782.5
	ν_9	540	716	723	719	725.5	546	551	540
	ν_{10}	323	326.5	326	394	396.5	383.5	385	323
E′	ν_{11}	2582	3485	3484	3486	3486	2594	2621	2582
	ν_{12}	1895	1897	1921	2520	2535	2519	2522	1895
	ν_{13}	1418	1440	1462	1465	1487.5	1438	1472	1418
	ν_{14}	1245	1328	1392	1406	1408	1289	1304	1245
	ν_{15}	797	1022	1030	1096	1102	1071	1075	797
	ν_{16}	766.5	813	816	990	1005	786	796	766.5
	ν_{17}	(499)	509	516	518	526	(507)	?	(499)
E″	ν_{18}	723	725	. . .	968	?	960	. . .	723
	ν_{19}	?	788	. . .	798	?	550	. . .	?
	ν_{20}	255	262	. . .	288	291	283	. . .	255

[a] Species A$_1$′ and E″ Raman lines, species A$_2$″ and E′ gas phase infrared spectra.

It is more difficult to justify the assignment of ν_8 of borazine at 917.5 cm^{-1}. Isotopic shifts should be opposite to those of ν_9; thus, for B-deuterated borazine, the γBD should be observed near 800 cm^{-1}. However, the absorption band structures in this region are rather complex (see Figure 1). Comparing the spectra of (–BH–NH–)$_3$ and (–^{10}BH–NH–)$_3$ it is evident that ν_8 of the former has an isotope band for γ^{10}BH at 927 cm^{-1}. However, the complexity of the corresponding bands in the spectra of B-deuterated borazines as illustrated in Figure 1 cannot result solely from the isotope effect. This conclusion is also reached by considering the band contours in the spectrum of (–^{10}BD–NH–)$_3$. In this case, the expected PQR branching of γ^{10}BD can clearly be seen but an overlapping with other bands is also evident. Therefore, the strongest bands of the complex structures observed near 800 cm^{-1} in the spectra of B-deuterated borazines are assigned to γBD and another at about 10 cm^{-1} higher frequency is assigned to γ^{10}BD.

	γBD, cm^{-1}	γ^{10}BD, cm^{-1}
(–BD–NH–)$_3$	808	817
(–^{10}BD–NH–)$_3$	. . .	819.5
(–BD–ND–)$_3$	782.5	792

Species E′.—All E′ vibrations are Raman and infrared active, although the Raman lines may be somewhat weak. There is no question about the validity of the original assignment of ν_{11} of borazine at 3496 cm^{-1}. Similarly, ν_{12} is fixed at 2520 cm^{-1} in agreement with earlier[2b,3] work. However, the two ring stretching vibrations (ν_{13} and ν_{14}) have previously been assigned at 1603 and 1465 cm^{-1}, respectively. The 1603 cm^{-1} absorption is now unequivocally identified as an impurity band (diborane). From an approximate coordinate treatment[20] it is evident that the electrooptical parameter $\Delta\mu_{BN}/\Delta r_{BN}$ should be extremely large for the high-frequency ring stretch (ν_{13}) and considerably smaller for ν_{14}. Therefore, the infrared intensities of the two vibrations should be $I(\nu_{13}) >> I(\nu_{14})$, and, indeed,

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(20) A more detailed discussion will be presented in a subsequent paper dealing with a normal coordinate treatment of borazines and a general valence force field of (–BH–NH–)$_3$.

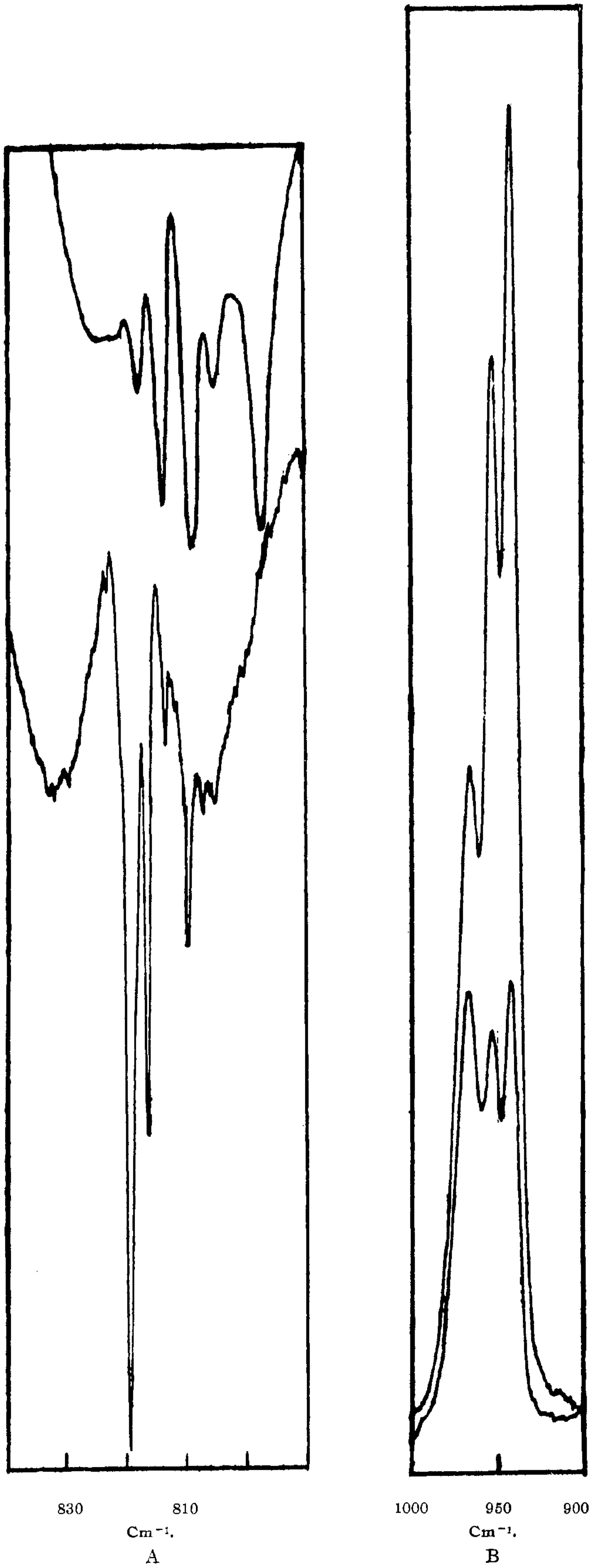

Figure 1.—A: The 790–840 cm^{-1} region of the infrared spectrum of $(-BD-NH-)_3$ (upper curve) and $(-{}^{10}BD-NH-)_3$ (lower curve). B: the 900–1000 cm^{-1} region of the Raman spectrum of $(-BH-ND-)_3$ (lower curve: polarization measurement).

in the spectra of all heterocyclic compounds containing the BN_2 entity, the highest BN stretching mode is normally the strongest band of the entire spectrum. Therefore, it is reasonable to assign the 1465 cm^{-1} absorption of borazine to ν_{13}.

In the Raman spectra of the isotopically labeled borazines, a depolarized line of about equal intensity to the Raman line of ν_{13} is observed in the 1220–1380 cm^{-1} region. These vibrations are too high to be considered as NH or BH deformational modes nor do they show the isotopic shifts expected for δNH or δBH modes. Accordingly, it seems reasonable to assign these lines to ν_{14}, particularly since they have counterparts in the infrared spectra (though they are at slightly higher frequencies in the gas phase spectra). The isotopic shifts of both, ν_{13} and ν_{14}, are as expected and the intensity relations of the infrared bands conform closely to the prediction reached by the normal coordinate treatment.

The assignment of ν_{17} at 518 cm^{-1} poses no problem; all isotope effects are minor but they follow the general pattern of the isotopic shifts observed for ν_{20} closely. The absorption of ν_{17} always appears as a weak infrared band, and in the spectra of $(-BH-ND-)_3$ and the corresponding boron-10 labeled compound, it is masked by the absorption of ν_9.

Therefore, only two modes of species E′ remain to be assigned, ν_{15} and ν_{16}. These two modes were assigned by Crawford and Edsall[2b] at 918 amd 718 cm^{-1}, respectively. As noted above, the assignment of the two modes was reversed by Kubo and co-workers.[5] However, in the present work these two frequencies have already been assigned to A_2'' vibrations of the borazine molecule according to the selection rules, band shapes, and isotopic shifts. The spectrum of borazine does not provide a conclusive answer as to where to look for the two E′ vibrations; but the weak band observed in the spectrum of N-trideuterioborazine near 786 cm.$^{-1}$ appears to have a counterpart in the spectrum of hexadeuterioborazine contained in the band structure near 780 cm^{-1} and appears to indicate the existence of a ND deformational mode. This assumption is reinforced by spectroscopic studies with isotopically labeled B-trichloroborazine[21] which clearly show that the NH deformation of species E′ in this compound should be assigned to the following frequencies: $(-BCl-NH-)_3$ = 1032 cm^{-1}, $(-{}^{10}BCl-NH-)_3$ = 1046 cm^{-1}, $(-BCl-ND-)_3$ = 816 cm^{-1}. Assuming similar shifts of this vibration in borazine upon N-deuteration, one can assign the NH deformation (E′) of borazine. Two infrared bands (at 994 and 1096 cm^{-1}, respectively) and one Raman line (1070 cm^{-1}) are observed in the spectrum of $(-BH-NH-)_3$. Although the difference $\Delta\nu = 1096 - 1070$ cm^{-1} is somewhat large, these two bands may represent the same vibration. However, a band of very similar shape is observed in the infrared spectrum of $(-BH-ND-)_3$ at 1071 cm^{-1}; therefore, this band must be considered as δBH rather than δNH. The corresponding δBD

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(21) To be published later.

mode can then be assigned to the 813 cm^{-1} peak in the spectrum of (-BD-NH-)$_3$ and to the 797 cm^{-1} absorption of (-BD-ND-)$_3$. Under these circumstances only the 994 cm^{-1} absorption of borazine remains for assignment to δNH. In the spectrum of (-BD-NH-)$_3$ a band of similar appearance is found at 1022 cm^{-1}. This shift to higher frequency may be readily interpreted by the coupling of the two deformational modes of the same species, and δND can be assigned at 786 cm^{-1} for (-BH-ND-)$_3$ and to one of the peaks (probably 767/775 cm^{-1}) of the complex band contour between 760 and 800 cm^{-1} in the spectrum of perdeuterated borazine.

The above assignments of the vibrations of species E$'$ are in agreement with the product rule. The band envelopes of some of the infrared bands of this species could be resolved. The band contours reveal that the Coriolis coupling constant for all E$'$ modes should be 0 ± 0.25 with the exception of ν_{17}. In this latter case, a marked Q branch is observed and $\Delta\nu_{PR}$ indicates a large negative ζ value.

Species E$''$.—The three vibrations of this species were assigned by Crawford and Edsall[2b] at 1070, 798, and 288 cm^{-1}, respectively. The lowest ring mode, ν_{20}, is primarily affected by B-deuteration (shift to 262 and 255 cm^{-1}, respectively), and, to a minor degree, by isotopically labeling the boron. Based on these observations, this mode appears to be satisfactorily identified.

A shoulder at the high-frequency side of ν_3 observed at 953 cm^{-1} was attributed by Hester and Scaife[19] to an isotope splitting (ν_3 = 940 cm^{-1}). A further line was observed by Goubeau and Gayoso[7] at 968 cm^{-1}. In the present work, these findings could be confirmed and the degree of polarization could be reliably measured in the case of (-BH-ND-)$_3$ (Figure 2). The Raman line shows three maxima at 940, 951, and 965 cm^{-1}, respectively. The two former are polarized but the latter is definitely depolarized and cannot be an additional isotope line. The corresponding bands of ν_3 in the spectra of B-deuterated borazines do not evidence any shoulders but new, depolarized Raman lines are observed at 725 and 723 cm^{-1}, respectively. In line with these observations, the cited frequencies can definitely be assigned to γBH (γBD).

Two possibilities exist for the assignment of the final E$''$ mode. As noted above, a considerable frequency difference between the Raman and the infrared bands is observed for δBH(E$'$). It is possible that the two bands are of different species and the 1070 cm^{-1} line is the missing E$''$ mode. Under these circumstances one of the weak Raman lines at 768 or 725 cm^{-1} in the spectrum of (-BH-ND-)$_3$ may be the corresponding γND vibration. No such line was observed in the spectrum of perdeuterated borazine. However, due to the small amount of material available, the spectrum of this latter compound was inferior in quality to those of the other isotopically labeled borazines studied in this work. Therefore, very weak lines might have escaped observation. On the other hand, the missing E$''$ mode may be assigned to the very weak Raman line at 798 cm^{-1} of borazine. However, a corresponding infrared band with an almost equivalent frequency has been observed. Since the frequency can hardly be interpreted as an E$'$ mode, it seems reasonable to attribute the infrared band to the combination $\nu_{17} + \nu_{20}$ (species A$_1''$ + A$_2''$ + E$''$), thus leaving the Raman line for assignment as a fundamental.

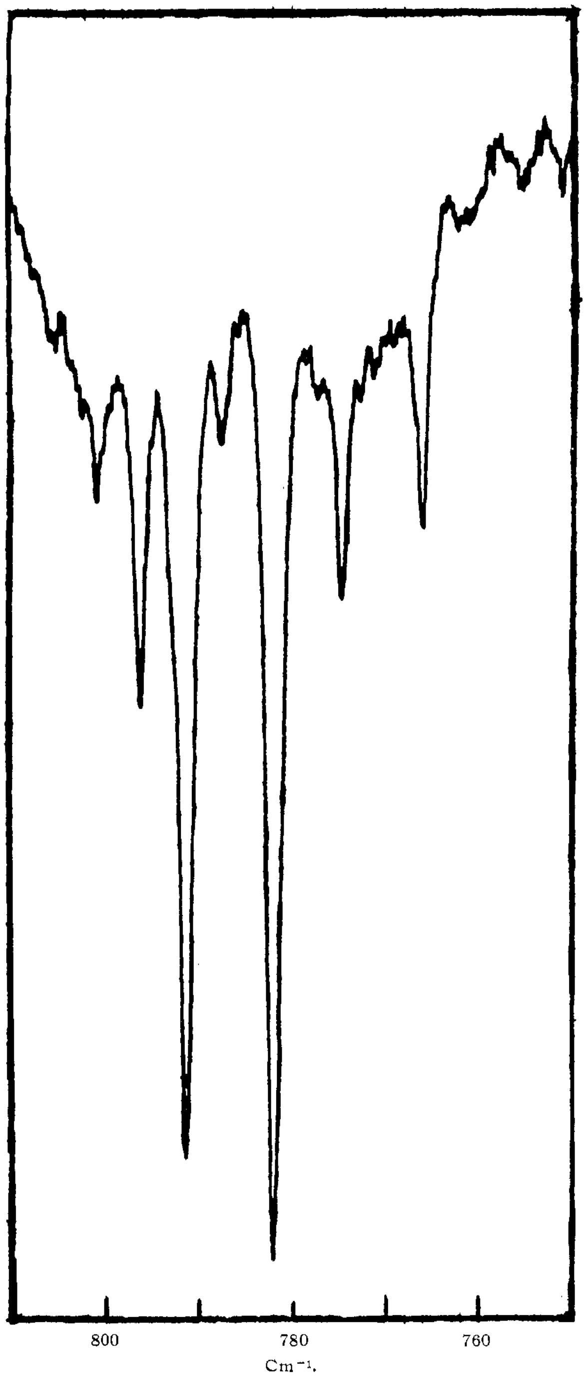

Figure 2.—The 750–810 cm^{-1} region of the infrared spectrum of (-BD-ND-)$_3$.

It should be noted that both assignments are in agreement with the Teller–Redlich product rule. However, the second interpretation appears to be preferable. The 1070 cm^{-1} frequency of borazine can reasonably be considered as an E′ mode, while no other explanation than E″ can be given for the 798 cm^{-1} line. Also, in the spectrum of B-trichloroborazine, the γNH(E″) mode is observed at 817 cm^{-1}.

Based on these assignments, the BH and NH deformational modes of species A_2'' and E″ show an appreciable correspondence in their frequency shifts upon deuteration, thus tending to support the validity of the assignments.

	γBH, cm^{-1}	γBD, cm^{-1}	γNH, cm^{-1}	γND, cm^{-1}
A_2''	~915	~795	~715	~545
E″	~965	~725	~790	~550

Conclusion

Table VII depicts the proposed assignments and the isotopic shifts of the borazine fundamentals. All other observed frequencies not assigned to fundamentals can be attributed to overtone and combination bands without making assumptions about the inactive A_1' vibrations or even those fundamentals which have some inherent uncertainty. From the data in Table VII it is apparent that most of the proposed assignment revisions of the vibrational frequencies of borazine are adequately substantiated by isotopic data, which are in agreement with the product rule. Nevertheless some minor uncertainties remain which should be clarified by a subsequent study of the vibrational spectra of substituted borazines. Also, a full mathematical treatment based on the present experimental data, which should permit more detailed descriptions of the vibrational character of the various modes, will be reported later.

The revised assignments of ν_{13} and ν_{14} should result in a lower B–N valence force constant of borazine than that heretofore assumed. It is apparent that the cited assignments of the two ring stretching modes of species E′ demand a reconsideration of the assignments made for the vibrational spectra of substituted borazines. The necessity for such study has already been indicated previously when these two modes of $(-BF-NH-)_3$ were identified at 1510 and 1401 cm^{-1}, respectively.[22] An examination of the available spectra of a large number of variously substituted borazines indicates that the strongest band of nearly all spectra (corresponding to the revised value of ν_{13} of the parent borazine) is always accompanied by a weaker absorption having a lower frequency of approximately 50–100 cm^{-1}. Such data are illustrated in Table VIII. B-Trifluoroborazine has the highest BN ring vibration of all borazines that have been studied to date.

TABLE VIII

THE TWO BN RING MODES (SPECIES E′) OF SOME BORAZINES

Borazine	BN ring modes, cm^{-1}	Borazine	BN ring modes, cm^{-1}
$(-BF-NH-)_3$	1510/1401	$(-BCl-NH-)_3$	1442/1334
$(-BCD_3-NH-)_3$	1485–1362	$(-BCH_3-ND-)_3$	1441/1322
$(-BCH_3-NH-)_3$	1482–1378	$(-BBr-NH-)_3$	1436/1327
$(-BH-NH-)_3$	1465/1406	$(-BH-NCH_3-)_3$	1412/1314

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[22] H. Beyer, H. Jenne, J. B. Hynes, and K. Niedenzu, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 266.

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Lewis Acidity of Alanes. Interactions of Trimethylalane with Sulfides

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Solution calorimetric techniques have been employed to determine the enthalpies of formation of a number of sulfide–trimethylalane adducts in hexane. The enthalpies (in kcal/mole) found are: $S(CH_3)_2$, −16.69 ± 0.18; $(C_2H_5)_2S$, −16.75 ± 0.17; $H_2\overline{CSC}HCH_3$, −15.24 ± 0.17; $(CH_2)_3S$, −16.04 ± 0.18; $(CH_2)_4S$, −16.95 ± 0.18; $(CH_2)_5S$, −16.99 ± 0.20. Tensimetric determinations of the enthalpies of vaporization and dimerization of trimethylalane yielded +9.88 ± 0.06 and −20.40 ± 0.34 kcal/mole, respectively. The enthalpy of vaporization of $(CH_3)_3Al\cdot S(CH_3)_2$ was found to be +10.99 ± 0.36 kcal/mole. These values were used along with enthalpies of solution to correct the solution enthalpy of formation of $(CH_3)_3Al\cdot S(CH_3)_2$ to the gas phase, yielding $\Delta H_f(g) = -18.05 \pm 0.50$ kcal/mole.

Introduction

Although alkylalanes have been established as relatively strong Lewis acids, the literature contains only a limited amount of data on the enthalpies of molecular adduct formation. The gas-phase enthalpies of formation of adducts of trimethylalane with dimethyl sulfide[2] and dimethyl selenide[3] have been reported but adducts of amines, ethers, and phosphines were found to be too stable to study by this technique.[2] Toward trimethylalane the relative donor abilities of several Lewis bases have been assigned using the results of displacement reactions.[2,3] Calorimetric investigations of triethylalane interactions with amines, ethers, and sulfides have been reported,[4-6] but with the

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