torium, 5251 Elbach über Engelskirchen, West Germany ($LiAl(CH_3)_4$).

Reagents.—The ^7Li (1% Na) and ^6Li were obtained from Lithium Corp. of America and Oak Ridge National Laboratory, respectively. CH_3I and CD_3I (99.5% D) were obtained from Aldrich Chemical Co. and Stohler Isotope Chemicals, respectively. $Al(CH_3)_3$ was purchased from the Ethyl Corp. Diethyl ether and cyclopentane were dried by refluxing over the Na–K alloy and were stored on a vacuum line. $Hg(CH_3)_2$ and $Hg(CD_3)_2$ were synthesized by the method of Gilman and Brown.[15] $Zn(CH_3)_2$ and $Zn(CD_3)_2$ were prepared by the reaction of $Hg(CH_3)_2$ or $Hg(CD_3)_2$ with Zn powder (Matheson Coleman and Bell) at 90° in the presence of a catalytic amount of $HgCl_2$. $Al(CD_3)_3$ was synthesized by refluxing $Hg(CD_3)_2$ with Al dust (Baker and Adamson) at 90°.[9] CH_3Li and CD_3Li were synthesized by the reaction of ^6Li or ^7Li (washed in cyclohexane, fivefold excess) with $Hg(CH_3)_2$ or $Hg(CD_3)_2$ in ether. The ether solutions of methyllithium (*ca.* 0.5 *M*) were filtered and used directly.

Preparation of Lithium Tetramethylzincate.—The $^6Li_2Zn(CH_3)_4$, $^7Li_2Zn(CH_3)_4$, and $^7Li_2Zn(CD_3)_4$ were synthesized by adding $Zn(CH_3)_2$ or $Zn(CD_3)_2$ (*ca.* 20% excess) to the ether solution of $^6LiCH_3$ or $^7LiCD_3$.[2,10] The solution was allowed to stand at room temperature overnight. The excess dimethylzinc and ether were removed under vacuum and the residue was evacuated at 50° for 2 hr under high vacuum.[2] *Anal.* Calcd for $^6Li_2ZnC_4H_{12}$: C, 34.94; H, 8.80; Zn, 47.54. Found: C, 34.94; H, 8.66; Zn, 47.76.

Preparation of Lithium Tetramethylaluminate.—The $^7LiAl(CH_3)_4$, $^6LiAl(CH_3)_4$, and $^6LiAl(CD_3)_4$ were synthesized by the reaction of $Al(CH_3)_3$ or $Al(CD_3)_3$ (*ca.* 50% excess) with $^6LiCH_3$, $^7LiCH_3$, or $^6LiCD_3$ in ether.[16] The mixture was allowed to stand at room temperature for 5 hr. The ether and excess trimethylaluminum were removed and the residue was evacuated at 80–90° for 5 hr under high vacuum, mp 273° dec (lit.[11] mp 260° dec). *Anal.* Calcd for $^7LiAlC_4H_{12}$: C, 51.10; H, 12.87; Al, 28.69. Found: C, 50.46; H, 12.52; Al, 27.29.

Infrared Spectra.—Infrared spectra in the range 4000–100 cm^{-1} were measured on a Beckman IR-12 (4000–200 cm^{-1}) and a Hitachi Perkin-Elmer FIS-3 (400–33 cm^{-1}) spectrophotometer. The IR-12 was calibrated with polystyrene; the FIS-3, with Teflon. The frequencies below 400 cm^{-1} reported in this study are those recorded on the far-infrared spectrophotometer. The Nujol technique with CsI plates (4000–200 cm^{-1}) or polyethylene plates (400–100 cm^{-1}) was employed for all compounds. In addition, the $Li_2Zn(CH_3)_4$ and $LiAl(CH_3)_4$ samples were studied as mulls in perfluorokerosene in the region 1300–4000 cm^{-1} to eliminate complications for C–H bands in the mulling agent.

The ir samples were prepared and loaded into cells in a drybox. In spite of these precautions some bands observed in the range 1000–1200 cm^{-1} varied in relative intensity in successive runs. These were most prominent for $Li_2Zn(CH_3)_4$ and are probably from hydrolysis or oxidation occurring during sample preparation or spectral determination. To minimize this difficulty, spectra were run several times on different preparations. Additionally, the samples were exposed to the air for 2–4 sec and the spectra were recorded again to observe the behavior of each band.[6] The bands associated with decomposition became very intense but the bands not due to decomposition became weaker and broader. Compared to lithium tetramethylzincate, lithium tetramethylaluminate was more stable to the air. The far-infrared spectra were all measured under vacuum.

To determine the frequencies, the infrared spectra were run on an expanded frequency scale with a scanning speed of 2–3 cm^{-1}/min. Reproducibility of the spectra was checked by multiple scans over the desired frequency range. The average error in frequency reading was ±0.5 cm^{-1}.

Raman Spectra.—Raman spectra of solid samples were measured on a Spex Ramalog Model 1401 with a Coherent Radiation Model 54 argon ion laser source. The spectrometer was calibrated with CCl_4.

The capillary tube for the Raman measurement was evacuated, placed in a drybox, and filled with a suitable amount of the sample (fine powder). The open end of the tube was closed with grease. The tube was removed from the drybox and immediately sealed with a small flame.

To determine the frequencies, the Raman spectra were run on an expanded frequency scale with a scanning speed of 10–20 cm^{-1}/min. The average error in frequency reading was ±1 cm^{-1}.

Nmr Spectra.—Nmr spectra were obtained on a Varian A-60-A spectrometer.

Acknowledgment.—The partial support of the Marquette University Committee on Research is gratefully acknowledged.

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[16] D. T. Hurd, *J. Org. Chem.*, **13**, 711 (1948).

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Vibrational Spectra of *B*-Trihaloborazines

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The vibrational spectra of *B*-trihaloborazines, $(-BX-NH-)_3$, with X = Cl or Br, have been examined and an assignment of the fundamentals is proposed. The data are supported by data obtained from isotopically labeled derivatives and a normal-coordinate treatment.

Introduction

Recently[2] the vibrational spectrum of borazine, $(-BH-NH-)_3$, has been reexamined utilizing data from isotopically labeled derivatives. This study resulted in the revision of assignments for some of the fundamental vibrations of borazine. Based on these data, a valence force field has been calculated; the resultant information confirms the suggested reassignments and the calculated force constants agree with recent considerations on the strength of the bonds in the borazine molecule.[3] The potential energy distribution of the isotopically labeled derivatives indicated that the character of several fundamentals is substantially altered by deuteration at either the boron or the nitrogen

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[1] (a) University of Kentucky. (b) University of Stuttgart. (c) Shionogi Research Laboratory. (d) Deceased.

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Table I

Vibrational Spectrum of *B*-Trichloroborazine (cm^{-1})[a]

(–BCl–NH–)$_3$			(–^{10}BCl–NH–)$_3$		(–BCl–ND–)$_3$			(–^{10}BCl–ND–)$_3$
Raman (solid)	Ir (solid)	Ir (soln)	Ir (solid)	Ir (soln)	Raman (solid)	Ir (solid)	Ir (soln)	Ir (soln)
	3445 ms	3506 ms	3447 ms	3434 s				
3412 vs						2569 s	2565 s	2575 s
					2539 vs			2533 vs
	2310 w	2300 w, b	2280 w					
	1886 vw	1898 vw	1903 vw					
	1773 vw	1795 vw	1795 vw				1789 w	1778 vw
							1641 w	1661 vw
	1606 vw		1604 w	1607 vw				
				1475 sh			1459 sh	1471 s
	1456 sh	1467 sh	1468 vs	1464 vs				
1445 w	1443 vs	1441 vs	1457 sh	1445 w		1430 sh	1425 s	1443 vs
						1414 vs	1407 vs	
	1375 wm	1375 m	1376 ms	1377 ms				
1350 w								
	1334 m	1334 m	1343 m	1342 m				1331 vw
								1295 s
						1281 m	1280 ms	1280 m
			1272 w	1269 w		1270 w	1265 w	
	1250 sh					1255 ms	1254 s	1260 m
			1237 m	1234 m		1240 w	1238 w	
					1223 m	1223 m	1222 m	
1214 wm	1216 wm	1217 wm	1211 vw					
							1174 w	1179 w
				1133 vw			1146 w	1148 vw
1122 wm	1117 vw							
	1094 vw							
			1074 w	1076 vw			1079 w	1079 w
	1044 vw		1045 s	1045 s				
	1039 sh	1038 sh	1034 sh	1035 wm				
	1032 ms	1031 s						
							965 w	973 s
860 s					828 s			
							820 sh	823 s
817 w						816 ms	815 s	
	791 vw		804 w					
	751 sh	750 sh	755 m	758 s		749 w	743 sh	
	743 s	741 ms	748 wm	750 s		739 s	736 s	743 s
	729 sh	726 wm	718 sh	733 w		722 w	718 wm	724 m
	706 s	704 ms	703 s	705 s				
							680 sh	671 s
	656 sh	652 sh	668 w	666 mw		662 m	658 ms	
	648 m	644 w				654 ms	651 s	
640 w								
			566 w	565 w			559 vw	
						503 s	502 s	505 s
			480 vw	482 w				
378 m	376 s	371 m	376 ms	373 m		367 m	360 m	
				360 w				
358 vs					357 vs			
							290 w	294 w
	274 w						280 m	286 w
							249 w	258 m
	181 m		182 w			182 m		
172 vw	172 s		170 m		169 s	170 s		
148 vw	147 vw				145 sh			

[a] Abbreviations: w, weak; m, medium; s, strong; v, very; sh, shoulder; b, broad.

atoms. Therefore, it seemed appropriate to extend the investigation of vibrational spectra to other selected borazine derivatives.

In the following work the vibrational spectra of symmetrical *B*-trihaloborazines, (–BX–NH–)$_3$, are discussed and particular attention is devoted to the spectrum of *B*-trichloroborazine, the most available of the haloborazines. In order to study the effect of a different halogen bonded to the boron atoms of a borazine ring, the spectrum of *B*-tribromoborazine has also been examined.

The structure of *B*-trichloroborazine has been studied by X-ray analysis[4] and by electron diffraction.[5] The infrared spectrum of the compound has been investigated repeatedly[6–8] but only equivocal assignments of some fundamentals have been made; the Raman spectra of *B*-trihaloborazines[9] have also been reported previously.

The results of the present spectroscopic study are substantiated by comparison with the observations of isotopically labeled derivatives; the resultant data help to clarify discrepancies with respect to previous assign-

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(9) R. E. Hester and C. W. J. Scaife, *ibid.*, **22**, 455 (1966).

ments within the vibrational spectrum of *B*-trichloroborazine. The assignment of fundamentals was greatly facilitated by a normal-coordinate treatment.

Experimental Procedures

B-Trichloroborazine was obtained by a modified[10] Brown–Laubengayer synthesis[11] by the reaction of boron trichloride with ammonium chloride. Boron-10-labeled derivatives and *N*-deuterio compounds were prepared as previously described.[2]

B-Tribromoborazine and its isotopically labeled derivatives were synthesized in a manner analogous to that used to obtain the corresponding chlorine compounds.

Infrared spectra of the various materials were recorded in the 33–4000-cm^{-1} range from the solids, from solutions in carbon tetrachloride and in carbon disulfide, and from mulls in Nujol and Kel-F polymer oil. The instruments used included Beckman IR-11 and IR-12 spectrometers, a Perkin-Elmer Model 621 double-beam infrared spectrophotometer, and a Japan Spectroscopic Co. DS-402G instrument, all used under standard operating conditions.

Raman spectra were obtained from the solids and from solutions in carbon disulfide with a Cary Model 81 Raman spectrometer and with a Jarrell-Ash double monochromator using a Spectrophysics argon laser as the exciting device. In all cases the frequency values listed in the tables are the averages of several recordings.

Calculations were performed on an IBM 360-50 digital computer at the University of Kentucky Computing Center. The programs, which use the Wilson *FG* technique[12] for setting up the vibrational secular equation, were written by Schachtschneider.[13]

Assignment of Fundamentals for *B*-Trichloroborazine

The *B*-trihaloborazine molecules appear to have D_{3h} symmetry. However, in the crystals, the site symmetry of *B*-trichloroborazine has been shown to be only C_s or C_1 and there is more than one molecule in the unit cell.[4,14,15] This circumstance may cause crystal field effects such as splitting of degenerate species which can result in a charge of selection rules.

As a basis for the present discussion, the representation for point group D_{3h} was used: $4\ A_1' + 3\ A_2' + 3\ A_2'' + 7\ E' + 3\ E''$. The activities of the fundamentals (see Table III) are analogous to those described for the parent borazine.[2] The spectra recorded on *B*-trichloroborazines are listed in Table I.

Species A_1'.—The assignment of ν_1, ν_3, and ν_4 of *B*-trichloroborazine poses no problems; the strongest Raman lines having no counterpart in the infrared spectrum are readily interpreted as A_1' modes. Furthermore, calculated fundamentals and the distribution of potential energy among the internal coordinates of *B*-trichloroborazine have been reported previously.[6] These data compare favorably with the experimental observations by Hester and Scaife[9] and their assignment of the three observed A_1' modes. The present calculations show that ν_2 should be observed near 1340 cm^{-1}. Therefore, it appears that ν_2 should be assigned to a weak Raman line observed in the spectrum of *B*-trichloroborazine at 1350 cm^{-1} (see Table I). This line lacks a counterpart in the infrared spectrum, and, on comparison with the data obtained on the parent borazine,[2,3] this frequency appears to be too high to be assigned to an E'' mode. Alternatively, ν_2 may be assigned to the Raman line observed at 1122 cm^{-1}; the resultant discrepancy between calculated and observed values for this mode could then be due to the fact that the force field used in the present calculations does not contain an interaction constant between the BN and BX valence vibrations. On the other hand, the general agreement between all the respective calculated and assigned values seems to indicate that the present force field is quite adequate. Calculated and observed values for the A_1' modes of *B*-trichloroborazine are listed in Table II.

TABLE II

THE A_1' MODES OF *B*-TRICHLOROBORAZINE (CM^{-1})

	Calcd				Obsd	
	Ref 9	Ref 9	Ref 6	This work	Ref 9	This work
ν_1	3340	3340	3433	3445	3411	3412
ν_2	1577	1250	1348	1338	. . .	1350
ν_3	837	842	844	854	858	860
ν_4	501	316	347	344	358	368

Species A_2''.—On comparison with the corresponding spectral data on borazine,[2] the three infrared-active A_2'' vibrations should be observed below 1000 cm^{-1} in the spectra of all *B*-trihaloborazines. The effects of N-deuteration permit ready assignment of the out-of-plane NH bending mode of *B*-trichloroborazine at 706 cm^{-1}. It is difficult to locate the remaining two vibrations of species A_2'' and normal-coordinate calculations were used as a primary guide for their proper assignment. Since the calculations indicated that the Raman line observed at 640 cm^{-1} in the spectrum of *B*-trichloroborazine should be assigned to an E'' mode, the infrared absorption at 648 cm^{-1} may well be one of the A_2'' fundamentals. This proposed assignment is in good agreement with the data of the normal-coordinate analysis. A small upward shift indicates some change in character of this mode upon deuteration at the nitrogen atoms in consonance with corresponding findings derived from deuteration of the parent borazine.[3]

Davies and Goldstein[16] reported an infrared absorption at 117 cm^{-1} in the spectrum of *B*-trichloroborazine. This band was not evident in our spectrum. However, this frequency seems to be a good selection for ν_{10} though our calculations suggest an even lower value for this mode.

Species E'.—Though vibrations of this species are both infrared and Raman active, the intensity of the Raman lines of species E' may be quite low as has previously been observed in the study of the vibrational spectrum of borazine.[2] However, N-deuteration permits the ready assignment of ν_{11}.

One of the most important results of the previous study on the parent borazine[2] involved the identification of the highest BN ring stretching mode at 1465 cm^{-1}. This vibration appears as one of the strongest bands in the entire spectrum, whereas the lower BN ring stretch found near 1400 cm^{-1} is of considerably lower intensity. Based on the observed boron isotopic shifts and the foregoing intensity considerations, the highest BN ring mode of *B*-trichloroborazine has been assigned at 1443 cm^{-1}. The identification of ν_{13} is complicated by the multiplicity of the spectra in the 1150–1400-cm^{-1} region. There appear to be two alter-

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[14] M. A. Viswanitra and S. N. Vaidya, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **121**, 472 (1965).

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natives for the assignment of this lower BN ring stretch in the spectra of *B*-trihaloborazines. It may be associated with bands near 1300 cm^{-1} (which exhibit clear isotope effects) or else with absorptions near 1200 cm^{-1} (of virtually constant frequency). The former assignment is preferred since the corresponding mode of the parent borazine exhibits an isotope shift analogous to that observed for the 1334-cm^{-1} band of *B*-trichloroborazine. Furthermore, the results of the normal-coordinate analysis lend credence to this assignment by disclosing a calculated frequency of 1321 cm^{-1} for this mode.

In the spectra of $(-BX-NH-)_3$, with X = Cl or Br, an infrared band is consistently observed near 1030 cm^{-1}; upon deuteration of the molecule at the nitrogen atoms, the absorption shifts to about 810 cm^{-1}. This band remains to be assigned to δ(NH) (E′) since the only other infrared-active NH deformation has already been assigned at 706 cm^{-1}. This assignment of ν_{14} to the 810-cm^{-1} band tends to support the previous assignment[2] of δ(NH) (E′) in the spectrum of borazine near 1000 cm^{-1} which was found to be in agreement with the data derived from a normal-coordinate treatment of the molecule.[3] It should be noted that the 1032-cm^{-1} band of *B*-trichloroborazine exhibits a marked boron isotope shift thereby indicating some contribution from internal movements of the boron atoms.

The assignment of ν(BCl) (E′) at 743 cm^{-1} is supported by the observed isotopic shift ($\nu(^{10}BCl)$ at 748 cm^{-1}). The two remaining E′ vibrations are identified by simultaneous observations of Raman lines and infrared absorptions at 376 and 172 cm^{-1}, respectively. In view of the magnitude of the shifts to lower frequencies with increasing atomic weights of the halogen substituents in *B*-trihaloborazines, the lower of these two frequencies is considered to have more of δ(BX) character. This view is supported by the calculated distribution of potential energy among these modes.

Species E″.—Due to the low quality of the Raman spectra of the *B*-trihaloborazines, which are all solids under normal conditions, certain Raman lines may have escaped observation. This assumption is substantiated by the fact that even the E″ Raman lines of the parent borazine molecule are of moderate intensity.[2] However, the normal-coordinate calculations lend support to the suggested assignments of the observed Raman lines as depicted in Table III.

The Vibrational Spectrum of *B*-Tribromoborazine

The vibrational spectra of *B*-tribromoborazine and isotopically labeled derivatives thereof are listed in Table IV. These spectra are very similar to those obtained on *B*-trichloroborazine and the fundamentals of *B*-tribromoborazine can be assigned readily on the basis of the preceding discussion.

It is noteworthy that bromine and chlorine bonded to boron in borazines appear to have little effect on the NH vibrations. The latter appear virtually unaffected by the mass of the halogen atoms and are found to have almost identical frequencies as is the case with borazine.

Two of the A_1' frequencies, ν_1 and ν_3, are remarkably constant in their location indicating that of the two ring vibrations, ν_3 is virtually a pure breathing motion of the nitrogen atoms. The other one, ν_4, is a breathing of the boron atoms; both ν_3 and ν_4 interact with the stretching mode of the corresponding ligand atom.

TABLE III

CALCULATED AND OBSERVED FUNDAMENTALS OF *B*-TRICHLOROBORAZINE (CM^{-1})

Modes Species (activity)		$(-BCl-NH-)_3$		$(-^{10}BCl-NH-)_3$		$(-BCl-ND-)_3$		$(-^{10}BCl-ND-)_3$	
		Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
A_1' (R)	ν_1	3445	3412	3445	...	2542	2539	2542	...
	ν_2	1329	1350	1378	...	1326	...	1375	...
	ν_3	854	860	854	...	821	828	821	...
	ν_4	345	358	346	...	345	357	346	...
A_2'' (ir)	ν_8	711	706	711	703	508	503	510	505
	ν_9	650	648	665	668	659	654	673	671
	ν_{10}	87	117[a]	88	...	85	...	86	...
E′ (R, ir)	ν_{11}	3443	3445	3443	3447	2537	2569	2537	2575
	ν_{12}	1446	1443	1477	1468	1419	1414	1454	1443
	ν_{13}	1321	1334	1354	1343	1260	1255	1296	1260
	ν_{14}	1033	1032	1042	1045	818	816	824	823
	ν_{15}	748	743	753	748	714	739	715	743
	ν_{16}	371	376	373	376	362	367	364	...
	ν_{17}	173	172	174	170	172	170	172	...
E″ (R)	ν_{18}	804	817	808	...	737	...	749	...
	ν_{19}	639	640	653	...	528	...	535	...
	ν_{20}	150	148	151	...	141	145	142	...
Av error, %		2.4		0.8		1.3		1.5	
$\Delta\nu$, cm^{-1}		8.5		5.4		8.8		17.2	

[a] From ref 16.

These findings are in agreement with the observations on borazine[2] and the results of an approximate normal-coordinate treatment[9] as well as the present normal-coordinate analysis.

The distinct energy difference between the NH stretching mode near 3420 cm^{-1} and the nitrogen breathing at 860 cm^{-1} permits unequivocal assignment of these modes. However, due to the strong interaction of vibrations involving boron atoms, both ν_2 and ν_4 appear to represent a mixture of boron–halogen stretching and boron breathing.

Assignments of the in-plane vibrations are reasonably well substantiated and the assignment of δ(NH) (E′) tends to support the assignment of this mode in the parent borazine near 1000 cm^{-1}.[2]

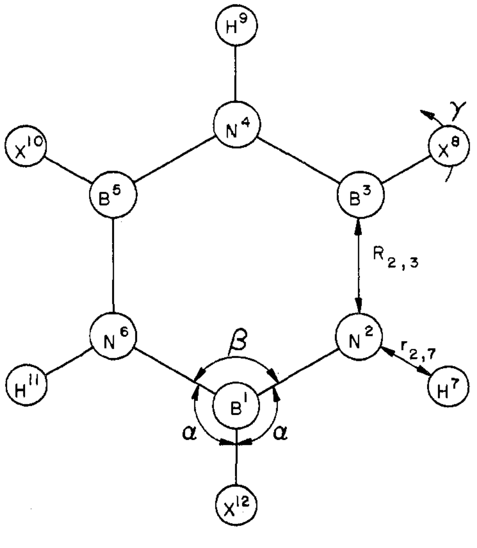

Figure 1.—Internal coordinates of *B*-trihaloborazines.

The masses of chlorine and bromine are both relatively large and the displacements of the atoms seem to be quite small. This situation is illustrated by the similarity of the spectra of *B*-trichloroborazine and *B*-tribromoborazine. Most deviations from the basic trend of frequencies can qualitatively be interpreted by a simple mass effect or by the coupling of vibrational

TABLE IV

VIBRATIONAL SPECTRUM OF *B*-TRIBROMOBORAZINE (CM^{-1})[a]

$(\text{-BBr-NH-})_3$			$(\text{-}^{10}\text{BBr-NH-})_3$		$(\text{-BBr-ND-})_3$			$(\text{-}^{10}\text{BBr-ND-})_3$
Raman (solid)	Ir (solid)	Ir (soln)	Ir (solid)	Ir (soln)	Raman (solid)	Ir (solid)	Ir (soln)	Ir (soln)
3432 sh	3466 s	3446 s	3465 ms	3421 s		3445 w	3440 vw	
3420 ms								
						2532 ms	2545 s	2560 s
					2530 m			2525 m
		2286 vw		2286 vw			2232 vw	2244 vw
							2070 vw	2100 vw
		1883 vw		1890 vw				
								1732 vw
		1657 vw		1675 w			1638 w	1643 w
		1528 w						1507 w
							1497 wm	
	1450 sh	1445 sh	1465 vs	1461 vs				
1436 vw	1436 vs	1436 vs						1440 vs
						1424 sh	1426 s	1419 sh
				1404 sh		1404 vs	1404 vs	1405 sh
			1392 m	1385 s				
	1377 s	1379 s		1369 s		1362 w	1362 wm	1356 wm
	1327 m	1327 m		1344 ms			1333 w	1330 vw
						1272 vw	1272 sh	1271 s
						1265 vw	1265 ms	1259 ms
						1241 s	1241 vs	1241 sh
	1231 vw	1231 vw						
				1212 m				1219 m
						1208 vw	1205 wm	1204 sh
	1196 w	1196 wm				1188 w	1191 ms	1181 vw
	1170 vw	1167 vw						
	1093 vw	1093 vw				1085 vw	1085 w	1098 w
1074 vw								1074 w
	1044 vw	1046 wm				1060 vw	1060 vw	1053 w
1040 vw	1039 sh	1038 s, sh	1040 vs	1038 s				
	1025 vs	1024 vs		1030 sh		1033 vw	1033 vw	
859 s					829 s	806 m	808 ms	812 s
		795 wm						
		787 w						
		767 w						
	704 s	703 s	708 s	706 s		703 w	705 wm	716 wm
	678 sh	677 sh	682 ms	678 s			672 sh	677 ms
672 vw	665 s	667 s				664 ms	660 s	670 sh
	640 w	638 w	641 m	652 ms		646 m	626 wm	653 ms
	628 m	632 m				632 sh	635 m	
607 vw								
570 vw								
						507 m	506 ms	507 ms
		346 vw				340 vw	340 w	
316 wm	316 ms	316 m	315 s	305 w	308 w	309 m	298 w	299 w
		290 w						
228 vs					225 s			
	210 vw		208 vw			198 vw		
153 wm					145 w			
112 vs	116 w		117 w		110 vs	111 w		
	97 vw		111 vw					

[a] See footnote *a* of Table I.

modes. There is no conclusive evidence that mesomeric or inductive effects contribute to the electronic structure of the borazine ring in *B*-trihaloborazines.

Calculated and observed values for the fundamentals of *B*-tribromoborazines are listed in Table V. In Table VI, the observed fundamentals of those *B*-trihaloborazines studied are compared with those of the parent borazine illustrating the frequency shifts upon substitution at the boron atoms of the heterocycle.

Normal-Coordinate Analysis

All bond angles were assumed to be 120°, a value of 1.413 Å was taken for the BN bond distance, and the NH and BX distances of 1.01 and 1.754 Å, respectively, were used.

Forty-two internal coordinates were constructed using the notation as depicted in Figure 1. In the resultant representation, redundancies were removed by methods discussed by Schachtschneider.[13] Symmetry coordinates were constructed by standard procedures.[12]

The potential energy function is given by

$$2U = \sum_{i=1}^{10} N_i K_i (\delta q_i)^2 + \sum_{i \neq j} N_{ij} K_{ij} (\delta q_i)(\delta q_j)$$

where U is the potential energy, N is the number of internal coordinates constituting an equivalent set, K is the force constant, and q is the internal coordinate. The second term in this expression is summed over 23 interaction coordinates the nature of which is depicted in Table VII. It can be noted that contributions to the potential energy for all interactions are positive; this necessitates the careful construction of the out-of-plane internal coordinates and the force constant matrix.

TABLE V

CALCULATED AND OBSERVED FUNDAMENTALS OF *B*-TRIBROMOBORAZINE (CM^{-1})

Modes Species (activity)		(–BBr–NH–)$_3$ Calcd	(–BBr–NH–)$_3$ Obsd	(–^{10}BBr–NH–)$_3$ Calcd	(–^{10}BBr–NH–)$_3$ Obsd	(–BBr–ND–)$_3$ Calcd	(–BBr–ND–)$_3$ Obsd	(–^{10}BBr–ND–)$_3$ Calcd	(–^{10}BBr–ND–)$_3$ Obsd
A_1' (R)	ν_1	3448	3420	3448	. . .	2544	2530	2544	. . .
	ν_2	1285	. . .	1333	. . .	1281	. . .	1329	. . .
	ν_3	857	859	858	. . .	824	829	825	. . .
	ν_4	221	228	222	. . .	221	225	222	. . .
A_2''	ν_8	710	704	710	708	507	507	509	507
	ν_9	646	628	659	641	659	646	671	653
	ν_{10}	54	. . .	54	. . .	52	. . .	53	. . .
E' (R, ir)	ν_{11}	3445	3466	3445	3465	2538	2532	2539	2560
	ν_{12}	1440	1436	1468	1465	1407	1404	1439	1440
	ν_{13}	1317	1327	1349	1344	1246	1241	1282	1259
	ν_{14}	1027	1025	1039	1038	801	806	806	812
	ν_{15}	699	665	705	682	684	664	688	677
	ν_{16}	315	316	318	315	307	309	309	. . .
	ν_{17}	119	116	119	117	118	111	118	. . .
E'' (R)	ν_{18}	801	. . .	803	. . .	720	. . .	728	. . .
	ν_{19}	608	607	622	. . .	515	. . .	523	. . .
	ν_{20}	148	153	149	. . .	138	145	139	. . .
Av error, %		1.9		1.1		1.6		1.2	
$\Delta\nu$, cm^{-1}		12.7		8.6		9.1		11.6	

For example, the relative positive or negative character of the internal coordinates involved in a torsion—out-of-plane wagging interaction must correspond with the sign of the element in the force constant matrix in order to obtain the correct positive contribution to the potential energy function.

The primary objective of the normal-coordinate analysis of *B*-trihaloborazines was to clarify the situation with respect to the assignment of several fundamentals, to test the significance of interaction constants, and to describe the normal vibrations as accurately as possible. It is worth noting that the frequency calculations provide useful guidance for suggested assignments in those cases where spectral data were inconclusive as discussed in the preceding section.

TABLE VII

FORCE CONSTANTS OF *B*-TRICHLOROBORAZINE[a]

No.	Description	Value	Estd error
	A. Valence Force Constants		
1	B–N str	4.9052	±0.0681
2	B–X str	3.9159	±0.0
3	N–H str	6.5026	±0.0
4	Planar B–X bend	0.9397	±0.0
5	Planar N–H bend	0.3271	±0.0
6	NBN ring distortion	1.2242	±0.0
7	BNB ring distortion	1.2000	±0.0
8	Nonplanar B–X bend	0.2216	±0.0
9	Nonplanar N–H bend	0.2846	±0.0
10	B–N torsion	0.3105	±0.2500
	B. Interaction Force Constants		
11	B^1–N^2 str—N^2–B^3 str	0.5169	±0.0
12	B^1–N^2 str—B^1–N^6 str	0.2500	±0.0
13	B^1–N^2 str—B^3–N^4 str	−0.1187	±0.0942
14	B^1–N^2 str—B^4–N^5 str	0.0596	±0.0
15	Planar B^1–X bend—B^1–X str	0.2305	±0.0
16	Planar N^2–H bend—N^2–H	−0.2006	±0.0039
17	Planar B^1–X bend—B^1–N^2 str	0.5845	±0.1458
18	Planar B^2–H bend—N^2–B^3 str	0.2752	±0.2026
19	Planar B^1–X bend—B^1–N^6 str	−0.1339	±0.0643
20	Planar N^2–H bend—N^2–B^1 str	−0.0686	±0.0279
21	N^{2}B^{1}N^6 ring distortion—B^{1}N^{2}B^3 ring distortion	0.2467	±0.0
22	N^{2}B^{1}N^6 ring distortion—N^{2}B^{3}N^4 ring distortion	0.1303	±0.0
23	N^{2}B^{1}N^6 ring distortion—B–N str	0.1083	±0.0
24	B^{1}N^{2}B^3 ring distortion—N^2–B^3 str	0.1206	±0.0
25	Planar N^{2}B^{1}X bend—planar N^{6}B^{1}X bend	0.0733	±0.0423
26	Planar B^{1}N^{2}H bend—planar B^{3}N^{2}H bend	−0.0584	±0.0150
27	Planar N^{2}B^{1}X bend—planar B^{1}N^{2}H bend	−0.2454	±0.0235
28	B^{1}N^2 torsion—nonplanar B^1–X bend	−0.0509	±0.0976
29	B^{1}N^2 torsion—nonplanar N^2–H bend	−0.0758	±0.0673
30	Nonplanar B^1–X bend—nonplanar N^2–H	0.0331	±0.0300
31	B^{1}N^2 torsion—N^{2}B^3 torsion	−0.0612	±0.0550
32	B^{1}N^2 torsion—B^{3}N^4 torsion	0.2326	±0.2010
33	B^{1}N^2 torsion—N^{4}B^5 torsion	−0.4388	±0.0821

[a] Stretching in mdyn/Å; bending in mdyn Å/radian^2; stretch—bend interactions in mdyn/radian.

A total of 33 force constants was included within the valence force field, including 23 interaction force constants. The latter were selected by analogy to the criteria used for the normal-coordinate calculations of borazine.[3] The final valence force field in this latter work was arrived at through a regression procedure. In the present work it is assumed that the reported[3] force field adequately reflects that of *B*-trihaloborazines. This assumption is born out by the rapid convergence between observed and calculated frequencies of (–BCl–NH–)$_3$ and (–BBr–NH–)$_3$. In performing the calculations, a set of trial diagonal force constants was adjusted using the interaction force constants from a previous[3] study. After perturbation, the interaction

TABLE VI

SUGGESTED ASSIGNMENTS AND DESCRIPTION OF FUNDAMENTALS OF *B*-TRIHALOBORAZINES COMPARED WITH THE PARENT BORAZINE[a]

Modes		(–BH–NH–)$_3$	(–BD–NH–)$_3$	(–BCl–NH–)$_3$	(–BBr–NH–)$_3$	(–BH–ND–)$_3$	(–BD–ND–)$_3$	(–BCl–ND–)$_3$	(–BBr–ND–)$_3$
ν_1	ν_s(NH)	3452	3452	3412	3420	2579	2567	2539	2430
ν_2	ν_s(BX)	2535	1893	1350	. . .	2521	1895	. . .	. . .
ν_3	ν_s(BN, ring)	940	903	860	859	940	901	828	829
ν_4	δ_s(BN, ring)	852	852	358	228	824	824	357	225
ν_8	γ(NH)	719	716	706	704	546	540	503	507
ν_9	γ(BX)	917	808	648	628	900	782	654	646
ν_{10}	γ(BN, ring)	394	326	117[b]	. . .	384	323	. . .	. . .
ν_{11}	ν_{as}(NH)	3486	3485	3446	3466	2594	2582	2569	2532
ν_{12}	ν_{as}(BN, ring)	1465	1440	1443	1436	1438	1418	1414	1404
ν_{13}	ν_{as}(BN, ring)	1406	1328	1334	1327	1289	1245	1255	1241
ν_{14}	δ(NH)	990	1022	1032	1025	786	766	816	806
ν_{15}	ν_{as}(BX)	2520	1897	743	665	2519	1895	739	664
ν_{16}	δ(BN, ring)	518	509	376	316	507	499	367	309
ν_{17}	δ(BX)	1096	813	172	114	1071	797	170	111
ν_{18}	γ(NH)	798	725	817	. . .	550		. . .	. . .
ν_{19}	γ(BX)	968	788	640	607	960		. . .	. . .
ν_{20}	γ(BN, ring)	288	262	148	153	283	255	145	145

[a] Frequencies in cm^{-1}; numbering of fundamentals for *B*-trihaloborazine. [b] From ref 16.

TABLE VIII

FORCE CONSTANTS OF $(\text{-BBr-NH-})_3$[a]

No.	$(\text{-BBr-NH-})_3$ Calcd value	$(\text{-BBr-NH-})_3$ Estd error	Stacked calcn[b] Calcd value	Stacked calcn[b] Estd error
	A. Valence Force Constant			
1	4.8561	±0.0779	4.883	±0.0575
2	3.2890	±0.0	3.381	±0.0023
3	6.5122	±0.0	6.503	±0.0007
4	0.8823	±0.0	0.8821	±0.0
5	0.3454	±0.0	0.3435	±0.0001
6	1.4178	±0.0	1.3736	±0.0025
7	1.1709	±0.0395	1.1709	±0.0
8	0.2284	±0.0	0.2665	±0.0
9	0.2793	±0.0	0.2796	±0.0
10	0.3633	±0.2420	0.1932	±0.1500
	B. Interaction Force Constants			
11	0.5326	±0.0	0.6808	±0.0
12	0.2500	±0.0	0.7233	±0.2296
13	−0.1555	±0.1227	0.0031	±0.0
14	0.1230	±0.0	−0.0012	±0.0
15	0.2668	±0.0	0.4999	±0.1056
16	−0.1996	±0.0002	−0.1720	±0.0068
17	0.6104	±0.1273	0.8001	±0.0727
18	0.2864	±0.2742	0.5676	±0.0
19	−0.1479	±0.0644	0.1742	±0.0516
20	−0.0596	±0.0970	0.0739	±0.0204
21	0.2467	±0.0	0.1821	±0.0
22	0.1303	±0.0	−0.0832	±0.0116
23	0.1083	±0.0	0.1083	±0.0
24	0.1206	±0.0	0.1206	±0.0
25	0.0717	±0.0	−0.0623	±0.0447
26	−0.0583	±0.0097	−0.0738	±0.0011
27	−0.2438	±0.0494	−0.3124	±0.0443
28	−0.1036	±0.2160	−0.0629	±0.0402
29	−0.0543	±0.0474	−0.0460	±0.0572
30	0.0621	±0.0569	0.0686	±0.0165
31	−0.0737	±0.0451	0.0326	±0.1002
32	0.2822	±0.0254	0.1375	±0.4817
33	−0.4941	±0.0359	−0.3304	±0.0223

[a] For descriptions and units of force constants, see Table VII.
[b] See text for details.

force constants were refined in a similar manner by holding the diagonal force constants fixed and, subsequently, by simultaneous adjustment. The weights utilized in the least-squares adjustment were set equal to $1/\lambda$ where λ was the observed frequency being fitted.

The final force constants are depicted in Tables VII and VIII. Error estimates were obtained from the force constant matrix resulting from the theory of least squares.[13] The frequency calculations as illustrated in Tables III and V are in good agreement with the experimental data which are further substantiated by product rule calculations. The potential energy distributions for the *B*-trihaloborazines are depicted in Table IX. It is noteworthy that the group frequency assignments as suggested in Table VI are in consonance with the potential energy distribution when the mode is assigned to the major contributing internal coordinate.

The degree of transferability between the force fields of *B*-trichloro- and *B*-tribromoborazine was studied by "stacking" the observed fundamentals of both derivatives along with that of the N-deuterated species and adjusting the force field to fit all of these data. The resultant force constants and the calculated frequencies are listed in Tables VIII and X, respectively. Numerical values of the force constants are about intermediate between those derived from the separate calculations; both calculated and observed frequencies are in good agreement. These results suggest that the bonding in *B*-trihaloborazines where the halogen is Cl or Br are quite similar and that spectral trends can be interpreted by simple mass effects.

Calculated frequencies for the A_2' modes of the *B*-trihaloborazines, which are Raman and infrared inactive, are listed in Table XI.

It is worth noting that upon least-squares adjust-

TABLE IX

POTENTIAL ENERGY DISTRIBUTION OF $(\text{-BX-NH-})_3$ ($X = Cl, Br$)

Planar modes		N-H str Cl	N-H str Br	B-X str Cl	B-X str Br	B-N str Cl	B-N str Br	B-X planar bend Cl	B-X planar bend Br	N-H planar bend Cl	N-H planar bend Br	NBN ring distortion Cl	NBN ring distortion Br	BNB ring distortion Cl	BNB ring distortion Br
A_1'	ν_1	0.99	0.99	...	...	...	...	...	...	...	...	...	...	...	...
	ν_2	...	...	0.40	0.32	0.16	0.15	0.07	0.08	0.03	0.03	0.19	0.26	0.19	0.22
	ν_3	0.01	...	0.03	0.04	0.48	0.54	0.07	0.05	0.03	0.02	0.19	0.18	0.19	0.15
	ν_4	...	...	0.57	0.65	0.25	0.20	0.02	...	...	...	0.04	0.03	0.04	0.03
E'	ν_{11}	0.99	0.99	...	...	...	...	...	...	...	...	...	...	...	...
	ν_{12}	...	...	0.19	0.12	0.43	0.42	0.05	0.05	0.25	0.31	0.13	0.15	0.02	0.02
	ν_{13}	...	...	...	...	0.71	0.70	0.14	0.12	0.10	0.12	0.02	0.02	0.09	0.10
	ν_{14}	...	...	0.14	0.10	0.30	0.38	0.05	0.06	0.53	0.46	0.02	0.03	0.01	0.01
	ν_{15}	...	...	0.38	0.35	0.41	0.36	0.06	0.07	0.02	0.04	0.04	0.10	0.15	0.20
	ν_{16}	...	...	0.25	0.36	0.14	0.13	0.15	0.18	0.10	0.09	0.34	0.30	0.27	0.21
	ν_{17}	...	...	0.02	0.05	0.12	0.11	1.13	1.11	0.11	0.09	0.02	...	0.06	0.03

Nonplanar modes		BX wag Cl	BX wag Br	NH wag Cl	NH wag Br	BN torsion Cl	BN torsion Br
A_2''	ν_8	0.04	0.04	1.38	1.38	0.25	0.35
	ν_9	0.40	0.40	0.14	0.10	2.16	2.48
	ν_{10}	1.02	4.13	0.7	1.82	...	1.92
E''	ν_{18}	0.06	0.04	1.02	1.03	0.24	0.23
	ν_{19}	0.24	0.28	0.08	0.04	0.47	0.69
	ν_{20}	0.78	0.98	0.01	0.10	0.07	...

Nonplanar modes		Interactions NH-BX Cl	NH-BX Br	BX-torsion Cl	BX-torsion Br	NH-torsion Cl	NH-torsion Br	Torsion-torsion, 31 Cl	Torsion-torsion, 31 Br	Torsion-torsion, 32 Cl	Torsion-torsion, 32 Br	Torsion-torsion, 33 Cl	Torsion-torsion, 33 Br
A_2''	ν_8	−0.13	−0.24	−0.05	−0.12	−0.42	−0.33	−0.10	−0.14	0.37	0.54	−0.35	−0.47
	ν_9	−0.13	−0.20	−0.51	−1.01	−0.40	−0.24	−0.85	−1.01	3.24	3.24	3.05	−3.37
	ν_{10}	−0.14	−2.70	0.09	−2.86	0.01	−0.90	...	−0.78	0.01	2.98	−0.01	−2.61
	ν_{18}	−0.07	−0.11	−0.06	−0.09	−0.31	−0.21	−0.05	−0.05	−0.18	−0.18	0.34	0.32
	ν_{19}	0.04	−0.05	−0.16	−0.39	0.12	0.07	−0.09	−0.14	−0.35	−0.53	0.55	0.93
	ν_{20}	−0.03	−0.15	0.11	0.05	0.02	...	−0.01	...	−0.05	...	0.10	...

TABLE X

TRANSFERABILITY OF FORCE FIELDS
(RESULTS OF STACKED FREQUENCY CALCULATIONS)

Modes Species (activity)		$(-BCl-NH-)_3$ Calcd	$(-BCl-NH-)_3$ Obsd	$(-BCl-ND-)_3$ Calcd	$(-BCl-ND-)_3$ Obsd	$(-BBr-NH-)_3$ Calcd	$(-BBr-NH-)_3$ Obsd	$(-BBr-ND-)_3$ Calcd	$(-BBr-ND-)_3$ Obsd
A_1 (R)	ν_1	3443	3412	2539	2539	3443	3420	2539	2530
	ν_2	1198	. . .	1197	. . .	1186	. . .	1186	. . .
	ν_3	862	860	828	828	862	859	827	829
	ν_4	338	358	338	357	227	228	227	225
A_2'' (ir)	ν_8	707	706	505	503	707	704	505	507
	ν_9	608	648	622	654	608	628	621	646
	ν_{10}	80	117	78	. . .	70	. . .	68	. . .
E′ (R, ir)	ν_{11}	3343	3345	2538	2569	3443	3466	2538	2532
	ν_{12}	1441	1443	1401	1414	1439	1436	1397	1404
	ν_{13}	1317	1334	1237	1255	1317	1327	1237	1241
	ν_{14}	1032	1032	805	816	1031	1025	803	806
	ν_{15}	713	743	711	739	684	665	682	664
	ν_{16}	373	376	364	367	316	316	306	309
	ν_{17}	167	172	165	170	120	116	199	111
E″ (R)	ν_{18}	801	817	722	. . .	801	. . .	722	. . .
	ν_{19}	616	640	524	. . .	616	607	524	. . .
	ν_{20}	154	148	144	145	149	153	138	145

TABLE XI

CALCULATED FREQUENCIES OF SPECIES A_2' FOR
B-TRIHALOBORAZINES (X = Cl, Br)

	$(-BX-NH-)_3$ Cl	$(-BX-NH-)_3$ Br	$(-BX-ND-)_3$ Cl	$(-BX-ND-)_3$ Br	$(-^{10}BX-NH-)_3$ Cl	$(-^{10}BX-NH-)_3$ Br	$(-^{10}BX-ND-)^3$ Cl	$(-^{10}BX-ND-)^3$ Br
ν_5	1339	1345	1172	1136	1359	1362	1201	1164
ν_6	1083	1055	988	992	1089	1063	989	992
ν_7	327	291	291	260	332	296	294	264

ment, the BN stretching force constant of borazine is reduced by replacing boron-bonded hydrogen by chlorine or bromine. On the other hand, upon B-halogenation the BN torsional force constant increases relative to the value obtained for the parent molecule.[3]

Discussion

Borazine, $(-BH-NH-)_3$, and its derivatives have often been compared with the isoelectronic benzene system. However, experimental justification for such comparisons has never been convincing. On the basis of the present data on *B*-trihaloborazines and the previous work[3] on borazine, some correlations of the two isoelectronic systems can be demonstrated.

The CC stretching force constant of benzene has been reported with a value of 7.832 mdyn/Å.[17] In borazine, the corresponding BN valence force constant is substantially lower with a value of 5.463 mdyn/Å. This difference, however, is to be expected since any π bonding within the borazine ring is effected solely by electrons from the nitrogen atoms. Therefore, the out-of-plane force constants might be more informative with respect to bonding analogies between the two cyclic isoelectronic systems. If this is true, the borazine and benzene systems are indeed similar as illustrated by the compilation of nonplanar force constants in Table XII.

TABLE XII

NONPLANAR FORCE CONSTANTS (MDYN/Å) OF
BORAZINES AND BENZENES[18,19]

	$(-BH—NH-)_3$–$(-CH=CH-)_3$		$(-BCl—NH-)_3$–$(-CCl=CH-)_3$
BH bend	0.517	BCl bend	0.222
CH bend	0.398	CCl bend	0.472
NH bend	0.322	CH bend	0.472
BN torsion	0.233	NH bend	0.285
CC torsion	0.181	BN torsion	0.311
		CC torsion	0.353

The CH bending force constant of benzene is intermediate between the BH and NH bending force constants of borazine. This trend is consistent with the arrangement of elements in the periodic table and may indicate comparable bonding environments in isoelectronic molecules. This assumption receives some support by the trend of the BCl and CCl bending force constants as shown in Table XII, which is also similar to that of the BCl and CCl stretching force constants in BCl_3 and CCl_4, respectively.[20,21] Furthermore, the frequency trends of the out-of-plane modes of *N*-trideuterioborazine[3] and *s*-trideuteriobenzene[18] correlate quite favorably.

Apparently, detailed investigations of the vibrational spectra of isoelectronic molecules reveal interesting factors with respect to the concept of isoelectronic systems.

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