

sidered as estimates. The lower reactivity of the ammine complex is due to unfavorable activation enthalpy. This is consistent with a degree of bond breaking being important for the aquoammine complex. The difference in reactivity of the aquocyanide complex with bromide and chloride, however, suggests that the entering ligand also plays a role in activation. The associative interchange mechanism thus may provide the best overall picture of the process.

The third-order rate constant for reaction 2 reported previously is $1.2 \times 10^5 M^{-2} \text{sec}^{-1}$ at 25° and $\mu = 1 M$, somewhat lower than that reported here. The

reason for this difference is not known. There are few additional data for comparison with the water-replacement rates reported here since many platinum(IV) reactions proceed by redox pathways involving platinum(II).⁹ This type of path appears excluded here because of the presence of excess bromine and, therefore, a very low concentration of platinum(II).

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Boron-Nitrogen Compounds. XL.^{1a} The Vibrational Spectrum of *B*-Trifluoroborazine

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The vibrational spectrum of *B*-trifluoroborazine, $(-\text{BF}-\text{NH}-)_3$, has been investigated and an assignment of fundamentals is proposed. The data are supported by a study of the infrared spectrum of $(-\text{BF}-\text{ND}-)_3$ and compare favorably with a normal-coordinate analysis of *B*-trifluoroborazine. The effect of boron-bonded fluorine on the electronic structure of the borazine ring is discussed.

Introduction

Recently, the vibrational spectra of borazine^{2,3} and some *B*-trihaloborazines⁴ were reinvestigated. The results of these studies suggested a smaller BN force constant than previously reported for borazines⁵⁻⁷ and also indicated that chlorine or bromine substitution at the boron sites exerts little or no mesomeric or inductive effects on the borazine ring system. Therefore, it seemed appropriate to extend this study to include the *B*-trifluoroborazine molecule. In this latter compound inductive effects should be most pronounced if they play any significant part in the nature of the BN ring bonding of borazines.

The structure of *B*-trifluoroborazine has been studied by electron diffraction⁸ and by X-ray analysis.⁹ The infrared spectrum in the sodium chloride region¹⁰ and the Raman spectrum¹¹ have been reported previously and these spectral data are in agreement with the results of the present investigation.

In the present work the infrared and Raman spectra of *B*-trifluoroborazine and the infrared spectrum of

its *N*-perdeuterated derivative are reported and assignments of the fundamental modes of vibration are suggested. The latter are in consonance with the results of a normal-coordinate analysis which also illustrates significant coupling of vibrations involving motions of the BF group.

Experimental Data

B-Trifluoroborazine, $(-\text{BF}-\text{NH}-)_3$, was prepared by the reaction of *B*-trichloroborazine with titanium tetrafluoride.¹² The *N*-perdeuterated compound was obtained from the dehydrofluorination of $\text{F}_3\text{B} \cdot \text{ND}_3$.¹³

Infrared spectra were recorded on the gas phase (10-cm cell with cesium iodide windows at autogeneous pressure and ambient temperature) and the solid material with a Perkin-Elmer Model 621 infrared spectrometer using cesium iodide windows.

The Raman spectrum of *B*-trifluoroborazine was obtained from the solid and from a solution in carbon disulfide with a Cary Model 81 Raman spectrometer and with a Jarrell-Ash double monochromator using a Spectrophysics 50-mW He-Ne laser operating at 6328 Å as the exciting device. In all cases the listed frequency values are the averages of several recordings and the instruments were operated at normal conditions.

Computer calculations were performed on an IBM 360-65 computer at the University of Kentucky Computing Center. The programs, which use the Wilson *FG* technique¹⁴ for setting up the vibrational secular equation, were written by Schachtschneider.¹⁵

Assignment of Fundamentals

In analogy to borazine, the *B*-trifluoroborazine molecule can be assumed to be planar and having D_{3h} symmetry. Recent X-ray work⁹ has illustrated, however,

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that solid *B*-trifluoroborazine has more than one molecule per unit cell and has a low site symmetry of C_s . This event may cause deviation from the selection rules for a D_{3h} model in the solid-state spectra and splitting of degenerate fundamentals can be expected. However, there is little spectral evidence for such an occurrence and it appears that solid *B*-trifluoroborazine consists of only weakly interacting molecules. This assumption is supported by the relatively high vapor pressure of the solid.

In the present work assignments of fundamentals were made on the basis of a D_{3h} model according to the representation $4 A_1' + 3 A_2' + 3 A_2'' + 7 E' + 3 E''$. The observed spectra are listed in Table I.

TABLE I
VIBRATIONAL SPECTRUM OF *B*-TRIFLUOROBORAZINE^a

Raman, solid	(-BF-NH-) ₃		(-BF-ND-) ₃
	Ir, solid	Ir, gas	Ir, gas
3440 vs	3445 ms	3478 ms	3480 vw
			2578 ms
	1524 sh	1524 sh	1506 sh
	1512 sh	1512 vs	1501 sh
1500 w	1495 vs	1506 vs	1491 vs
			1474 vs
	1397 w	1396 m	1401 sh
			1391 wm
			1362 w
1350 w		1328 wm	
	1307 vw		
1298 vw			1159 vw
1210 w	1207 w		
			1119 vw
1130 m	1139 ms	1137 ms	1025 m
			934 vw
927 vw	915 m	921 wm	
863 s			
	850 w		776 vw
820 wm			733 sh
	755 w	741 m	729 ms
	731 sh	738 s	723 sh
	725 s	729 s	718 ms
718 vw	717 s	721 sh	715 sh
		691 mw	
		671 sh	
		661 m	
		654 sh	
630 w			622 vw
551 vs			493 sh
			486 m
			484 sh
438 ms	438 s	435 vw	
			425 vw
375 w			
	335 m	336 vw	
300 w	293 s	289 vw	301 vw
178 m			
147 vw			

^a Frequencies in cm^{-1} . Key: w, weak; m, medium; s, strong; v, very; sh, shoulder.

Species A_1' .—The identification of ν_1 , ν_3 , and ν_4 poses no problems and these modes can readily be assigned on the basis of the observed spectra. Three strong Raman lines appear at 3440, 863, and 551 cm^{-1} , respectively, in consonance with earlier work.¹¹ In contrast, the assignment of ν_2 is difficult to accomplish. Previous data⁴ suggest that ν_2 of *B*-trichloroborazine occurs at 1350 cm^{-1} and, therefore, assignment of ν_2 to

the weak Raman line observed in the spectrum of *B*-trifluoroborazine at this same frequency is unlikely. This assumption is also supported by the fact that frequency calculations indicate that ν_2 of *B*-trifluoroborazine should be observed near 1500 cm^{-1} ; consequently, ν_2 has not been assigned in the present work.

Species A_2'' .—In the spectrum of *B*-trifluoroborazine all A_2'' fundamentals should occur below 1000 cm^{-1} . Moreover, vibrational bands of species A_2'' should exhibit a PQR structure with a prominent Q branch. These criteria suggest the assignment of the 729- cm^{-1} infrared band as an A_2'' mode. A structure similar to the 729- cm^{-1} band is exhibited by the 661- cm^{-1} absorption, the latter shifting to 486 cm^{-1} upon deuteration at the nitrogen sites of the molecule. The remaining A_2'' frequency, ν_{10} , was not observed. The calculated value for ν_{10} , 122 cm^{-1} , indicates that this mode should occur below the spectral range of the present study.

Species E' .—On the basis of a D_{3h} model, the seven E' fundamentals should be infrared and Raman active. Previous studies on borazines have shown that the Raman intensities of E' modes are frequently quite low.

The assignment of ν_{11} of *B*-trifluoroborazine can be made without difficulty to the infrared band observed at 3478 cm^{-1} . This band shifts to 2578 cm^{-1} upon deuteration at the nitrogen atoms. A major result of a previous study of borazine² resides in the reassignment of the highest BN stretching fundamental to 1465 cm^{-1} . In the infrared spectrum of *B*-trifluoroborazine several bands are recorded in the 1500- cm^{-1} region of which the 1506- cm^{-1} band has a definite counterpart in the Raman spectrum of the material. The second BN stretching mode, ν_{13} , is assigned to the infrared line of medium intensity observed at 1396 cm^{-1} . The Raman line at 1350 cm^{-1} might be interpreted as the counterpart to the latter although the frequency difference of 46 cm^{-1} appears to be somewhat large.

The significant frequency shift of the 1137- cm^{-1} infrared band to 1025 cm^{-1} upon N-deuteration suggests assignment of this vibration to a δ_{NH} mode. However, an even larger shift is observed for the infrared line at 921 cm^{-1} which has a counterpart in the spectrum of (-BF-ND-)₃ at 718 cm^{-1} . Consequently, these bands are assigned to ν_{14} and ν_{15} , respectively. Both involve motions of the nitrogen atoms, a factor which is clearly substantiated by the potential energy calculations. The latter also clearly reflect strong mixing of $\nu_{\text{BF}}(E')$ and $\delta_{\text{NH}}(E')$ and suggest that the 1137- cm^{-1} band has more ν_{BF} character.

The assignment of $\nu_{16}(\delta \text{ ring})$ is made on the basis of simultaneous observation of a Raman line and infrared band near 435 cm^{-1} . The potential energy distribution indicated that this mode involves 82% ring deformational character. The assignment of $\delta_{\text{BF}}(E')$ at 289 cm^{-1} is supported by the observation of an absorption of similar band shape in the spectrum of (-BF-ND-)₃ at 301 cm^{-1} . The calculated potential energy distribution indicates that this mode is comprised of 75% δ_{BF} character.

Species E'' .—Due to the fact that the Raman spectrum of *B*-trifluoroborazine is of low quality by nature since the material is solid under normal conditions, certain Raman lines may have escaped detection. However,

frequency calculations indicate about where the bands should appear in the Raman spectrum. The highest E'' fundamental, ν_{18} , is assigned to the medium-intensity Raman line at 820 cm^{-1} . This assignment corresponds with the assignments of the same mode in other B -trihaloborazines.⁴

There are two Raman lines, observed at 630 and 300 cm^{-1} , respectively, available for the assignment to ν_{19} . On the basis of the frequency calculations ν_{19} is assigned to the line of higher frequency since a frequency of 300 cm^{-1} is too low to be considered as $\delta_{\text{NF}}(E'')$ vibration. Finally, ν_{20} is assigned to the Raman line observed at 178 cm^{-1} . (See Table II.)

TABLE II
CALCULATED AND OBSERVED FREQUENCIES OF
 B -TRIFLUOROBORAZINE (cm^{-1})

Species (activity)	$(-\text{BF}-\text{NH}-)_3$			$(-\text{BF}-\text{ND}-)_3$		
	Obsd	Calcd	$\Delta\nu^a$	Obsd	Calcd	$\Delta\nu^b$
A_1' (R)	ν_1	3440	3469	29	...	2566
	ν_2	...	1474	1460
	ν_3	863	851	12	...	821
	ν_4	551	539	12	...	539
A_2'' (ir)	ν_5	729	756	27	729	712
	ν_6	661	664	3	486	511
	ν_{10}	...	122	121
E' (R, ir)	ν_{11}	3478	3466	12	2578	2556
	ν_{12}	1506	1514	8	1474	1477
	ν_{13}	1396	1406	10	1391	1386
	ν_{14}	1137	1130	7	1025	1038
	ν_{15}	921	909	12	718	721
	ν_{16}	435	435		425	427
	ν_{17}	289	297	8	314	297
E'' (R)	ν_{18}	820	784	36	...	617
	ν_{19}	630	618	11	...	551
	ν_{20}	178	153	25	...	144

^a Average error 14.5 cm^{-1} . ^b Average error 11.9 cm^{-1} .

Normal-Coordinate Analysis

In the present work all bond angles were taken to be 120° , and the experimentally determined bond distances⁹ are $\text{BF} = 1.34\text{ \AA}$ and $\text{BN} = 1.43\text{ \AA}$; NH was taken to be 1.02 \AA .³

In previous work on borazine³ and $(-\text{BCl}-\text{NH}-)_3$ and $(-\text{BBr}-\text{NH}-)_3$,⁴ interaction force constants were included in the final force field only after testing the significance of their contribution to the potential energy function which is presented by

$$U = \sum_{i=1}^{10} N_i K_i (\delta_{qi}) + \sum_{i \neq j} N_{ij} K_{ij} (\delta_{qi}) (\delta_{qj})$$

where U is the potential energy, N is the number of internal coordinates belonging to an equivalent set, K is the force constant, and q is the internal coordinate. This procedure is laborious and requires a number of least-squares adjustments on the modified force field under consideration. However, since the final force field used in previous work on B -trihaloborazines⁴ did not yield a satisfactory fit with the experimental data of B -trifluoroborazine upon least-squares adjustment when transferred, a modified force field was constructed by a regression procedure. In the least-squares adjustment, the weights were set equal to $1/\lambda$ where λ is the observed frequency being fitted. The final force field utilized in the present work is reflected in Table III. Numbering of atoms and the construction of internal coordinates are illustrated in Figure 1.

TABLE III
FORCE CONSTANTS OF TRIFLUOROBORAZINE^a

No.	Description	Value	Estd error ^b
A. Valence Force Constants			
1	B-N str	5.2307	0.0979
2	B-F str	5.2260	0.0000
3	N-H str	6.5876	0.0000
4	Planar B-F bend	0.9013	0.0000
5	Planar N-H bend	0.3721	0.0000
6	NBN ring distortion	1.6246	0.0000
7	BNB ring distortion	1.1547	0.0000
8	Nonplanar B-F bend	0.4410	0.0000
9	Nonplanar N-H bend	0.2984	0.0000
10	B-N torsion	0.2092	0.0000
B. Interaction Force Constants			
11	B^1-B^2 str— N^2-B^3 str	0.6386	0.0000
12	B^1-N^2 str— B^1-N^6 str	1.0426	0.0000
13	B^1-N^2 str— B^3-N^4 str	-0.4146	0.0000
14	B^1-N^2 str— B^4-N^6 str	-0.4242	0.0000
15	Planar N^2B^1F bend—planar N^6B^1F bend	-0.1077	0.0000
16	Planar B^1N^2H bend—planar B^3N^2H bend	-0.1922	0.0000
17	$N^2B^1N^6$ ring distortion— $B^1N^2B^3$ ring distortion	0.1948	0.0000
18	$N^2B^1N^6$ ring distortion— $N^2B^3N^4$ ring distortion	0.2455	0.0000
19	N^6B^1 str— B^1-F str	1.0319	0.0000
20	B^1N^2 torsion—nonplanar B^1-F bend	-0.0353	0.0000
21	B^1N^2 torsion—nonplanar N^2-H bend	-0.0954	0.0029
22	Nonplanar B^1-F bend—nonplanar N^2-H bend	-0.0087	0.0000
23	B^1N^2 torsion— N^2B^3 torsion	-0.0424	0.0000

^a Stretchings in mdyn/\AA ; bendings in mdyn \AA/radian^2 ; stretch—bend interactions in mdyn/radian . ^b Error estimates were obtained from the force constant matrix resulting from the theory of least squares.¹⁵

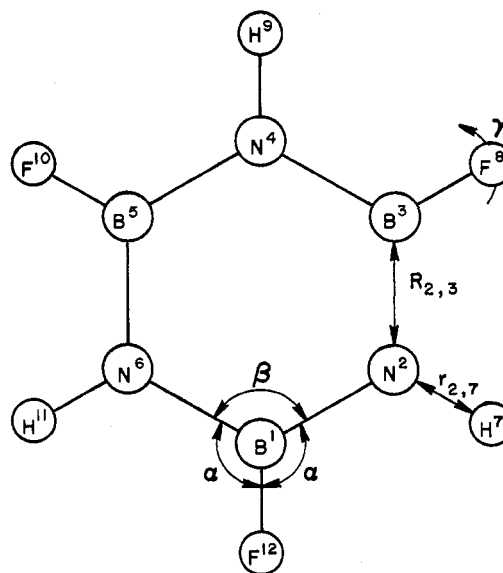


Figure 1.—Internal coordinates of B -trifluoroborazine.

The calculated potential energy distributions are listed in Table IV. Frequency assignments given in the preceding section of the present work are consistent with these data when the fundamentals are assigned to the major contributing internal coordinates.

It should be noted that the BN force constant is about the same as that reported for the parent borazine.³ Hence, it seems that the highly electronegative fluorine produces little or no mesomeric or inductive effects on

TABLE IV
 POTENTIAL ENERGY DISTRIBUTION OF $(-BF-NX-)_3$ (X = H, D)

Planar modes	N-H str		B-F str		B-N str		B-F planar bend		N-H planar bend		NBW ring distortion		BNB ring distortion		
	H	D	H	D	H	D	H	D	H	D	H	D	H	D	
A ₁ ' ν_1	0.99	0.96	0.01	...	0.01	...
ν_2	0.01	0.02	0.46	0.48	0.07	0.08	0.07	0.06	0.03	0.03	0.24	0.23	0.17	0.16	
ν_3	0.01	0.02	0.25	0.23	0.68	0.66	0.03	0.03	0.01	0.01	0.11	0.12	0.08	0.09	
ν_4	0.37	0.37	0.25	0.25	0.02	0.02	0.01	0.01	0.09	0.09	0.06	0.06	
E' ν_{11}	0.99	0.96	0.01	0.01	
ν_{12}	0.23	0.29	0.45	0.53	0.04	0.05	0.26	0.12	0.15	0.18	0.02	0.03	
ν_{13}	0.01	0.02	0.01	0.03	0.74	0.72	0.20	0.20	0.02	0.02	0.08	0.06	
ν_{14}	0.44	0.51	0.01	0.13	0.01	0.02	0.48	0.17	0.06	0.02	0.03	0.04	
ν_{15}	0.15	0.01	0.39	0.21	0.01	0.01	0.26	0.71	...	0.01	0.02	...	
ν_{16}	0.21	0.21	0.12	0.12	0.15	0.15	0.06	0.04	0.44	0.45	0.37	0.38	
ν_{17}	0.01	0.01	0.21	0.21	0.75	0.76	0.01	0.01	
Nonplanar modes		BF wag				NH wag				BN torsion					
A ₂ '' ν_8		H		D		H		D		H		D			
ν_8		0.33		0.83		1.34		0.68		0.53		1.26			
ν_9		0.58		0.07		0.03		0.73		0.79		0.05			
ν_{10}		0.16		0.16		0.64		0.60		2.21		2.22			
E'' ν_{18}		0.07		0.59		1.16		0.70		0.09		0.41			
ν_{19}		0.83		0.33		...		0.52		0.38		0.06			
ν_{20}		0.12		0.12		0.22		0.16		1.32		1.32			
Nonplanar modes		NH-BF interaction		BF-torsion interaction		NH-torsion interaction		Torsion-torsion interaction							
		H		D		H		D		H		D			
A ₂ '' ν_8		0.06		0.07		-0.21		-0.51		-0.14		-0.34			
ν_9		-0.01		-0.02		-0.32		-0.02		-0.22		-0.02			
ν_{10}		-0.01		-0.03		-0.90		-0.90		0.20		0.20			
E'' ν_{18}		0.01		0.03		-0.02		-0.08		-0.02		-0.14			
ν_{19}		...		-0.02		-0.08		-0.01		-0.16		-0.04			
ν_{20}			-0.27		-0.27		-0.12		-0.11			

the boron-nitrogen ring. A similar conclusion was reached in a study of *B*-trichloroborazine and *B*-tribromoborazine.³ Although the spectrum of *B*-trifluoroborazine on comparison with other borazines is different enough to suggest that fluorine atoms during molecular vibrations could affect the electronic structure of the borazine ring, this conclusion is not supported by the present data.

Discussion

The BN stretching mode of *B*-trifluoroborazine recorded at 1505 cm⁻¹ presents the highest such frequency observed for any borazine. However, this event cannot be constructed to imply a BN bond order significantly larger than that in other borazines. Rather, it merely reflects sizable coupling of BN modes with BF vibrations which is evident from the potential energy distribution of various fundamentals of the *B*-trifluoroborazine molecule. Indeed, the BN stretching force constant of the latter is even smaller than that of borazine. In Table V the force constants of borazine and three boron-halogenated derivatives thereof are listed. These data correlate favorably and seem to indicate that inductive effects of halogen on the

 TABLE V
 FORCE CONSTANT COMPARISON OF
 BORAZINE AND *B*-TRIHALOBORAZINES

Force constant no. ^a	(BHNH) ^b	(BFNH) ₃	(BCINH) ₃ ^c	(BBrNH) ₃ ^c
1	5.4623	5.2307	4.9052	4.8561
2	3.3499	5.2260	3.9159	3.2890
3	6.6677	6.5876	6.5026	6.5122
4	0.5544	0.9013	0.9397	0.8823
5	0.4592	0.3721	0.3271	0.3454
6	1.3450	1.6246	1.2242	1.4178
7	0.9085	1.1547	1.2000	1.1709
8	0.5170	0.4410	0.2216	0.2284
9	0.3316	0.2984	0.2846	0.2793
10	0.2325	0.2092	0.3105	0.3633

^a For description, see Table III. ^b From ref 3. ^c From ref 4.

electronic structure of the borazine ring are relatively minor. This conclusion is also substantiated by the frequency trends of comparable vibrations of borazines which, in general, are readily interpreted in terms of mass effects.

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