TABLE V

FUNDAMENTAL VIBRATIONS (CM^{-1}) IN B-MONAMINOBORAZINE

$H_3N_3B_3H_2NH_2$	$H_3N_3B_3H_2{}^{15}NH_2$	$H_3N_3B_3D_2ND_2$	Vibration species	Description
1612	1604	1275	A′	NH_2 def
1228	1227	1188		B–(NH_2) str
926	926	796		B–H bend
913	913	787		
725	719			NH_2 wag
677	677	673		N–H (ring) bend
3561	3552	2578	A″	NH_2 str
3482	3482	3483		N–H (ring) str
2521	2521	1884		B–H str
1483	1483	1492	Unassigned	B–N ring str
1451	1450	1431		B–N ring str
1395	1393	1366		B–N ring str

film spectra are shifted toward lower frequencies and features appear that are not observed in the gas spectra. The doublet at 3440 and 3405 cm^{-1} in the solid film spectrum probably results from an intermolecular splitting of the N–H (ring) vibrations, and the band at 3386 cm^{-1} is probably the counterpart of the in-phase N–H (NH_2 group) stretch in the gaseous molecule.

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A Vibrational Analysis of Gaseous Boroxine[1-3]

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With an improved method for the preparation of boroxine it has been possible to obtain infrared spectra of the gaseous compound at pressures up to 20 mm. Infrared spectra have been obtained for the isotopic species $H_3{}^{11}B_3{}^{16}O_3$, $H_3{}^{10}B_3{}^{16}O_3$, $H_3{}^{11}B_3{}^{18}O_3$, $D_3{}^{11}B_3{}^{16}O_3$, and $D_3{}^{11}B_3{}^{18}O_3$. The spectra are discussed in relation to two possible molecular structures: a planar model (D_{3h} configuration) and a nonplanar model (C_{3v} configuration). Spectral evidence from the partially deuterated species $H_2DB_3O_3$ and $HD_2B_3O_3$ support the nonplanar model and similarities between the spectra of boroxine and borazine are discussed. A normal-coordinate analysis based on several isotopic species yielded a set of simple valence force constants including one interaction constant, which could predict most of the observed vibrational frequencies to within 3%.

Introduction

Boroxine is a high-temperature molecule and at room temperature decomposes to B_2H_6 and B_2O_3 with a lifetime of from 10 min to 4 hr depending upon the surface condition of the vessel.[4,5] If the gas is condensed at liquid nitrogen temperature and then allowed to warm to room temperature, it decomposes to form diborane and boron oxide. Definite evidence for its existence was obtained by Sholette and Porter[6] from studies of the high-temperature reaction of H_2 and B–B_2O_3 in the mass spectrometer. Experiments by Lee, Bauer, and Wiberley[7] showed it to be an intermediate in the oxidation of pentaborane-9. The infrared spectrum of the solid was observed by Gupta and Porter in 1963.[8] Since then, two other independent investigations have reported a gas-phase infrared spectrum of low-pressure samples.[5,9] By the above procedures it was not possible to obtain pressures of boroxine above approximately 5 mm. Barton, Grimm, and Porter[10] found that much higher pressures of boroxine could be obtained by applying an electrical discharge to low-pressure diborane–oxygen mixtures. Using this technique we have obtained much stronger spectra, making it possible to reinvestigate the infrared spectrum for new absorption bands. From the observed frequencies a

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[1] Work supported by the Army Research Office, Durham, N. C., and the Advanced Research Projects Agency, Cornell University, Ithaca, N. Y.

[2] Taken in part from a thesis submitted by F. A. Grimm in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate School, Cornell University, Jan 1968.

[3] Thesis of F. A. G. Available from University Microfilms, Ann Arbor, Mich.

[4] J. F. Ditter and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 1022 (1959).

[5] S. K. Wason and R. F. Porter, *J. Phys. Chem.*, **68**, 1443 (1964).

[6] W. P. Sholette and R. F. Porter, *ibid.*, **67**, 177 (1963).

[7] G. H. Lee, W. H. Bauer, and S. E. Wiberley, *ibid.*, **67**, 1742 (1963).

[8] S. K. Gupta and R. F. Porter, *ibid.*, **67**, 1286 (1963).

[9] G. H. Lee, Ph.D. Thesis presented to the faculty of Rensselaer Polytechnic Institute, Troy, N. Y.

[10] L. Barton, F. A. Grimm, and R. F. Porter, *Inorg. Chem.*, **5**, 2076 (1966).

normal-coordinate calculation, assuming a planar molecule, gave a set of in-plane force constants, which could predict most of the observed frequencies for all isotopic species to within 3%.

Experimental Section

Boroxine was made by the technique of low-pressure explosions of diborane–oxygen mixtures as described previously.[10] These mixtures are highly unstable and should be handled with caution. Isotopically labeled species of boroxine were prepared by using combinations of B_2H_6, B_2D_6, and $^{10}B_2H_6$ with $^{16}O_2$ and $^{18}O_2$.[11] Diborane was obtained from the reaction of anhydrous stannous chloride and sodium borohydride[12] at 250°. The preparation of B_2D_6 used $NaBD_4$ obtained from Alfa Inorganics Inc. $^{10}B_2H_6$ was prepared by heating a small quantity of $CaF_2{}^{10}BF_3$ from Oak Ridge Laboratory with an excess of $LiAlH_4$. The gaseous products $^{10}BF_3$, $H^{10}BF_2$, $^{10}B_2H_6$, and H_2 were rapidly evolved when the solid mixture reached approximately 150°. Impurities were removed by adding a small quantity of ether, and $^{10}B_2H_6$, in low yield, was extracted by vacuum distillation.

Strong absorptions were measured using low-pressure spectra ($P_{\text{boroxine}} \sim$ 3mm). In this case the boroxine was prepared in a 350-ml Pyrex vessel. The weak absorptions were not detectable under these conditions and so required higher pressure samples. These were obtained by utilizing a long tube (volume ~700 ml) as the reaction vessel. Diborane (10 mm) and oxygen (10 mm) were admitted and allowed to mix for a few minutes. The explosion was initiated by applying a "Tesla" coil discharge, as before, and the products were swept into a 10-cm infrared gas cell (volume ~100 ml) by immediately opening one end of the tube to the cell and the other end to a large volume of argon at 1 atm pressure. By this means pressures estimated at approximately 15–20 mm of boroxine were obtained in the cell.

Spectra for all of the isotopic species were recorded on a Perkin-Elmer 337 Infracord spectrophotometer using KBr windows. The spectrum of naturally occurring boroxine, $H_2DB_3O_3$, $HD_2B_3O_3$, and $D_3B_3O_3$ were also recorded on a Perkin-Elmer Model 521 spectrophotometer down to 250 cm^{-1} using CsI windows. The molecules containing two hydrogens and one deuterium or one hydrogen and two deuteriums were prepared in the presence of the three hydrogen and three deuterium species by exploding mixtures of B_2H_6, B_2D_6, and O_2. In some instances, small concentrations of B_2H_6 were placed in an infrared cell in the reference beam to compensate for small amounts of unreacted material and to identify overlapping bands. Actual frequency measurements were checked against known values for absorption bands due to the impurities B_2H_6 and $HBCl_2$ sometimes present. BH_3CO and halosilanes were also present in very low concentrations.

Vibrational Assignments

The vibrational frequencies obtained for the various isotopes of boroxine are listed in Table I. Figures 1 and 2 show the infrared spectra for $H_3B_3{}^{16}O_3$ and $D_3B_3{}^{16}O_3$ which have the naturally occurring boron-10/boron-11 ratios. When preparing the $D_3B_3O_3$ molecule, it was impossible to eliminate hydrogen entirely from the system; however, statistical calculations show that the bands at 918 and 933 cm^{-1} in Figure 2 are too strong to be due to the negligible amount of $H_3B_3O_3$ present so these bands are attributed to the partially deuterated molecules (*i.e.*, $D_2HB_3{}^{16}O_3$). Spectra at higher pressures than those shown in Figures 1 and 2 were obtained by rapid scanning of small regions of the spectrum. In this way weak bands such as those at 990 and 760 cm^{-1} were made more prominent than those shown in the figures.

TABLE I

VIBRATIONAL FREQUENCIES AND ASSIGNMENTS

Freq, cm^{-1}	Intens	Symmetry class D_{3h}	Symmetry class C_{3v}	Description	Remarks
$H_3{}^{11}B_3{}^{16}O_3$					
2770	w	$2\nu_7$	$2\nu_9$	Overtone	2(1389) = 2778
2620	s	$\nu_6(E')$	$\nu_8(E)$	Asymmetric BH str	
2460	w	$2\nu_8$	$2\nu_{10}$	Overtone	2(1213) = 2426
1389	vs	$\nu_7(E')$	$\nu_9(E)$	Ring str	
1330	m	$\nu_{10} + \nu_3$	$\nu_{18} + \nu_4$	Combination	Assumed A_1 = 800 530 + 800 = 1330
1213	s	$\nu_8(E')$	$\nu_{10}(E)$	Ring str	
990	w	$\nu_9(E')$	$\nu_{11}(E)$	BH bend	
918	s	$\nu_{11}(A_2'')$	$\nu_2(A_1)$	BH bend	
530	m	$\nu_{10}(E')$	$\nu_{18}(E)$	Ring bend	
$H_3{}^{10}B_3{}^{16}O_3$					
2840	w	$2\nu_7$	$2\nu_9$	Overtone	2(1428) = 2856
2624	s	$\nu_6(E')$	$\nu_8(E)$	Asym BH str	
2510	w	$2\nu_8$	$2\nu_{10}$	Overtone	2(1228) = 2456
1428	vs	$\nu_7(E')$	$\nu_9(E)$	Ring str	
1340	m	$\nu_{10} + \nu_3$	$\nu_{13} + \nu_4$	Combination	Assumed A_1 = 803 537 + 803 = 1340
1228	s	$\nu_8(E')$	$\nu_{10}(E)$	Ring str	
1025	w	$\nu_9(E')$	$\nu_{11}(E)$	BH bend	
935	s	$\nu_{11}(A_2'')$	$\nu_2(A_1)$	BH bend	
537	m	$\nu_{10}(E')$	$\nu_{13}(E)$	Ring bend	
$D_3{}^{11}B_3{}^{16}O_3$					
2730	w	$2\nu_7$	$2\nu_9$	Overtone	2(1373) = 2746
2270	w	$2\nu_8$	$2\nu_{10}$	Overtone	2(1133) = 2266
1948	s	$\nu_6(E')$	$\nu_8(E)$	Asym BD str	
1373	vs	$\nu_7(E')$	$\nu_9(E)$	Ring str	
1321	m	$\nu_{10} + \nu_3$	$\nu_{13} + \nu_4$	Combination	Assumed A_1 = 800 522 + 800 = 1322
1133	s	$\nu_8(E')$	$\nu_{10}(E)$	Ring str	
808	s	$\nu_{11}(A_2'')$	$\nu_2(A_1)$	BD bend	
760	w	$\nu_9(E')$	$\nu_{11}(E)$	BD bend	
522	m	$\nu_{10}(E')$	$\nu_{18}(E)$	Ring bend	
$H_3{}^{11}B_3{}^{18}O_3$					
2720	w	$2\nu_7$	$2\nu_9$	Overtone	2(1365) = 2730
2610	s	$\nu_6(E')$	$\nu_8(E)$	Asym BH str	
2440	w	$2\nu_8$	$2\nu_{10}$	Overtone	2(1185) = 2370
1365	vs	$\nu_7(E')$	$\nu_9(E)$	Ring str	
1265	m	$\nu_{10} + \nu_3$	$\nu_{13} + \nu_4$	Combination	Assumed A_1 = 757 508 + 757 = 1265
1185	s	$\nu_8\ (E')$	$\nu_{10}(E)$	Ring str	
975	w	$\nu_9(E')$	$\nu_{11}(E)$	BH bend	
910	s	$\nu_{11}(A_2'')$	$\nu_2(A_1)$	BH bend	
508	m	$\nu_{10}(E')$	$\nu_{13}(E)$	Ring bend	
$D_3{}^{11}B_3{}^{16}O_3$					
2680	w	$2\nu_7$	$2\nu_9$	Overtone	2(1340) = 2680
2210	w	$2\nu_8$	$2\nu_{10}$	Overtone	2(1107) = 2214
1940	s	$\nu_6(E')$	$\nu_8(E)$	Asym BD str	
1340	vs	$\nu_7(E')$	$\nu_9(E)$	Ring str	
1260	m	$\nu_{10} + \nu_3$	$\nu_{13} + \nu_4$	Combination	Assumed A_1 = 757 503 + 757 = 1260
1107	s	$\nu_8(E')$	$\nu_{10}(E)$	Ring str	
803	s	$\nu_{11}(A_2'')$	$\nu_2(A_1)$	BD bend	
758	w	$\nu_9(E')$	$\nu_{11}(E)$	BD bend	
503	m	$\nu_{10}(E')$	$\nu_{13}(E)$	Ring bend	
$D_3{}^{10}B_3{}^{16}O_3$					
1974	s	$\nu_6(E')$	$\nu_8(E)$	Asym BD str	
1410	vs	$\nu_7(E')$	$\nu_9(E)$	Ring str	
832	s	$\nu_{11}(A_2'')$	$\nu_2(A_1)$	BD bend	
$H_3{}^{10}O_3{}^{18}O_3$					
928	s	$\nu_{11}(A_2'')$	$\nu_2(A_1)$	BH bend	
$D_3{}^{10}B_3{}^{18}O_3$					
810	s	$\nu_{11}(A_2'')$	$\nu_2(A_1)$	BD bend	

Since the geometrical structure of boroxine has not been determined, its symmetry group is unknown. Past investigators have assumed a planar molecule with D_{3h} symmetry and have justified the assumption by

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(11) The sample contained 92.5% ^{18}O and was obtained from YEDA, Research and Development Co., Rehovoth, Israel.

(12) W. Jeffers, *Chem. Ind.* (London), 431 (1961).

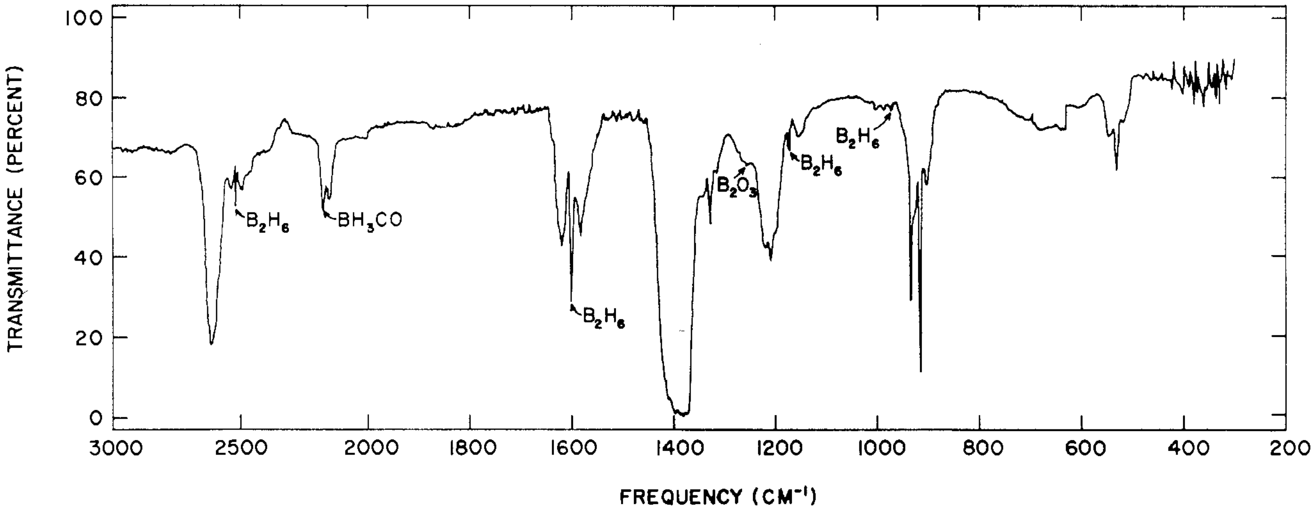

Figure 1.—Infrared spectrum of $H_3B_3{}^{16}O_3$.

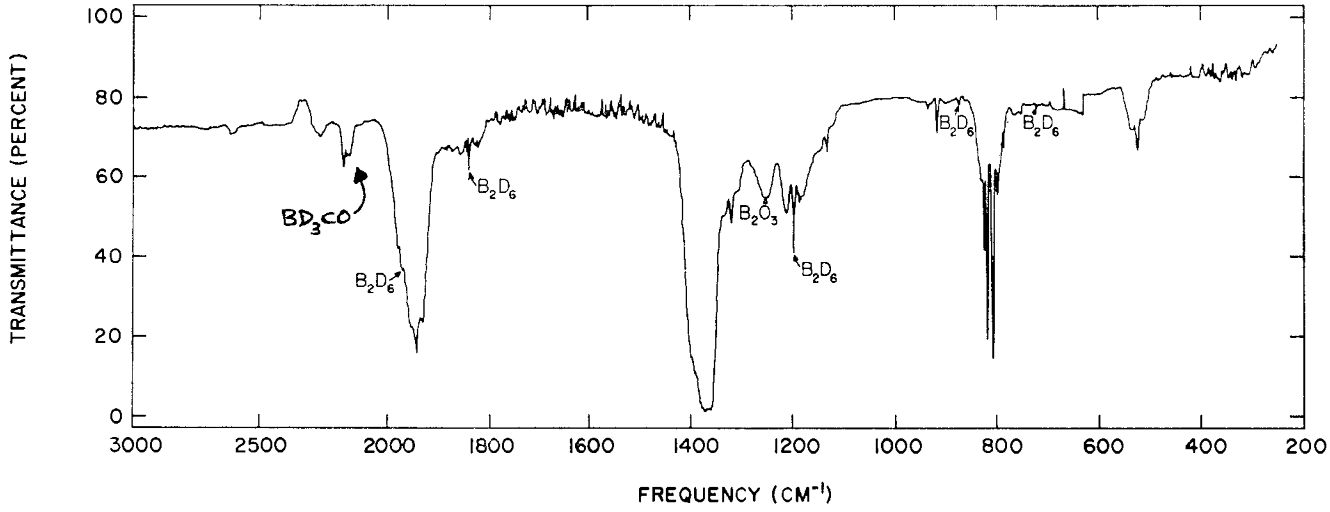

Figure 2.—Infrared spectrum of $D_3B_3{}^{16}O_3$.

analogy with borazine. The planarity of borazine has been based upon the early electron diffraction work done by Bauer,[13] in which the results were fitted to a D_{3h} model. The assignment for the vibrational frequencies of borazine, based upon this symmetry, has never been completely satisfactory.[14–17] The current dispute on borazine[16,17] poses the question of whether there is any sound basis for assuming boroxine to be a planar molecule. From nmr studies, which present some evidence for a threefold axis in borazine,[18] we may assume that there are two acceptable symmetry groups —either the planar configuration (D_{3h}) or the chair configuration (C_{3v}). It is of interest to compare the vibrational assignments based on each of these two symmetry groups.

Planar D_{3h} Symmetry Group.—In the case of D_{3h} symmetry, group theory[19,20] predicts the vibrational symmetry types

$$\Gamma_{\text{vib}} = 3\ A_1' + 2\ A_2' + 5\ E' + 2\ A_2'' + 2\ E''$$

of which there are ten Raman-active vibrations ($3\,A_1' + 5\ E' + 2\ E''$), two completely inactive vibrations ($2\ A_2'$), and seven infrared-active vibrations ($5\ E' + 2\ A_2''$).[19] Information on band contours may be useful in the assignments of the normal vibrations.[20] With the assumption of D_{3h} symmetry, boroxine is an oblate symmetric top with $I_A = 2I_B = 2I_C$. For this case vibrations of species A_2'' would be expected to have a PQR structure with a prominent Q branch. The separation of the maxima of the P and R branches for the parallel A_2'' vibrations can be estimated using a formula by Gerhard and Dennison[21] to be approximately 26 cm^{-1}. The shape of the band contours for the perpendicular E' vibrations depend upon the Coriolis coupling coefficients, which may be different

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[13] S. H. Bauer, *J. Am. Chem. Soc.*, **60**, 524 (1938).

[14] B. L. Crawford and J. J. Edsall, *J. Chem. Phys.*, **7**, 223 (1939).

[15] W. Watanabe, T. Totani, T. Nakagawa, and M. Kubo, *Spectrochim. Acta*, **16**, 1076 (1960).

[16] K. Niedenzu, W. Sawodny, H. Watanabe, J. W. Dawson, T. Totani, and W. Weber, *Inorg. Chem.*, **6**, 1453 (1967).

[17] V. B. Kartha, S. L. N. G. Krishnamachari, and C. R. Subramaniam, *J. Mol. Spectry.*, **23**, 149 (1967).

[18] Based on the proton spectrum of B-trideuterioborazine, unpublished work, Cornell University.

[19] E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

[20] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 2 D. Van Nostrand Co., Inc., Princeton, N. J., 1945.

[21] S. L. Gerhard and D. M. Dennison, *Phys. Rev.*, **43**, 197 (1933).

for each normal vibration.[20] Naturally occurring boron has two stable isotopes, ^{11}B and ^{10}B, which have a natural abundance of 80 and 20%, respectively. Therefore, boroxine would be expected to have four isotopic species, $H_3{}^{11}B_3O_3$, $H_3{}^{11}B_2{}^{10}BO_3$, $H_3{}^{11}B{}^{10}B_2O_3$, and $H_3{}^{10}B_3O_3$, in the ratio of approximately 64:48:12:1. The vibrations associated with BO ring modes should show a splitting due to these isotopic species and probably three of the four should be seen unless the band is very weak.[22] Using this and the following considerations the bands were assigned as follows.

E′ Species.—The five frequencies at 2620, 1389, 1213, 990, and 530 cm^{-1} are assigned as the E′ vibrations for the $H_3{}^{11}B_3{}^{16}O_3$ molecule. The assignment of the asymmetric BH stretch at 2620 cm^{-1} is obvious. The bands at 1389 and 530 cm^{-1} show very little shift upon deuterium substitution and are attributed to the ring stretching and bending modes, respectively. The other ring stretching mode is assigned at 1213 cm^{-1} and shows some deuterium shift. The 990-cm^{-1} band shows a large deuterium shift to 760 cm^{-1} and, therefore, would be the in-plane BH bending mode. Further proof for this assignment comes from an application of the Teller–Redlich product rule. Table II shows a comparison of the observed and predicted product ratios for some of the isotopic species studied.

Table II

D_{3h} Product Rule Calculations on E′ Vibrations

Ratio	Obsd	Calcd
$H_3{}^{10}B_3{}^{16}O_3/H_3{}^{11}B_3{}^{16}O_3$	1.09	1.080
$H_3{}^{11}B_3{}^{16}O_3/D_3{}^{11}B_3{}^{16}O_3$	1.931	1.965
$H_3{}^{11}B_3{}^{16}O_3/H_3{}^{11}B_3{}^{18}O_3$	1.110	1.088
$D_3{}^{11}B_3{}^{16}O_3/D_3{}^{11}B_3{}^{18}O_3$	1.096	1.088
$H_3{}^{11}B_3{}^{18}O_3/D_3{}^{11}B_3{}^{18}O_3$	1.906	1.933

A_2'' Species.—Only one of the A_2'' vibrations is assigned at 918 cm^{-1} to the out-of-plane BH bending mode. For the molecule containing boron-10, only one Q branch at 937 cm^{-1} is observed instead of the two Q branches at 918 and 933 cm^{-1}. The shape of the band and the separation of the P and R maxima seem to justify assigning this band as a parallel A_2'' vibration. The band structure on the 918 and 933-cm^{-1} regions is interesting in the sense that only two Q branches arising from the ^{10}B–^{11}B isotopic species are apparent while in the completely deuterated molecule the shifted band near 800 cm^{-1} shows three branches in the approximate intensities corresponding to the natural abundances of the $^{11}B_3$, $^{11}B_2{}^{10}B$, and $^{11}B^{10}B_2$ species. Wason and Porter[5] suggested that this effect in the $H_3B_3O_3$ molecule was due to a splitting of the Q branch in the $^{11}B_2{}^{10}B$ species into two components that accidentally overlap the branches of the $^{11}B^{10}B_2$ and $^{11}B_3$ species. It is possible that the band at 918 cm^{-1} is due only to $H_2{}^{11}B_3O_3$ and the band at 933 cm^{-1} is due to a coincidence of the branches for $H_3{}^{11}B_2{}^{10}BO_3$ and $H_3{}^{10}B_2{}^{11}BO_3$. However with this latter explanation it is somewhat difficult to account for the low intensity of the 933-cm^{-1} band (relative to the 918-cm^{-1} band) in low-pressure spectra.[5] In mixtures of partially deuterated species the region around 800 cm^{-1} shows as many as six Q branches. Figure 3 shows the effect obtained in these mixed deuterium–hydrogen species. By comparison of these spectra, it is possible to assign the many Q branches to one or more of the four species, $D_3B_3O_3$, $D_2HB_3O_3$, $DH_2B_3O_3$, and $H_3B_3O_3$, and the results of these assignments are summarized in Table III. Species like $D_2HB_3O_3$ can be further broken down depending upon whether the deuterium or hydrogen is on a ^{10}B or a ^{11}B, but further assignment of the bands to these various isotopes is not possible at the present time. The assignment of these bands will be discussed later.

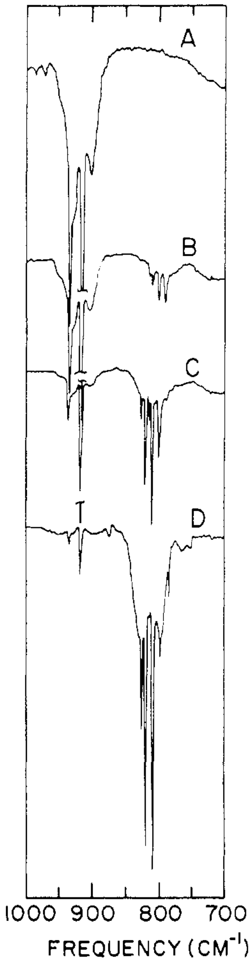

Figure 3.—The 800-cm^{-1} region of the infrared spectrum showing the effect of partial deuteration (boron contained the natural isotopic abundances): (A) prepared from 10.5 mm of B_2H_6 and 11 mm of O_2 (major $H_3B_3O_3$); (B) prepared from 8 mm of B_2H_6, 2.5 mm of B_2D_6, and 11 mm of O_2 (major species $H_2DB_3O_3$); (C) prepared from 2.5 mm of B_2H_6, 8 mm of B_2D_6, and 11 mm of O_2 (major species $HD_2B_3O_3$); (D) prepared from 10.5 mm of B_2D_6 and 11 mm of O_2 (major species $D_3B_3O_3$).

Overtone and Combination Bands.—For the D_{3h} symmetry group certain bands in the spectrum are tentatively assigned as overtones or combination bands and the results are included in Table I. The relatively strong combination band at 1330 cm^{-1} has been

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[22] W. C. Price, R. D. B. Fraser, T. S. Robinson, and H. C. Longuet-Higgins, *Discussions Faraday Soc.*, **9**, 131 (1950).

TABLE III

ASSIGNMENT OF THE Q BRANCHES IN THE 800- AND 900-CM^{-1} REGION FOR $H_3B_3O_3$, $H_2DB_3O_3$, $HD_2B_3O_3$, AND $D_3B_3O_3$ MOLECULES

Molecule	Freq, cm^{-1}
$H_3B_3O_3$	933, 918
$H_2DB_3O_3$	933, 918, 797, 786
$HD_2B_3O_3$	933, 918, 811, 797
$D_3B_3O_3$	824, 818, 808, 783

assigned as a combination of the E′ at 530 cm^{-1} and the unobserved A_1' species near 800 cm^{-1} ($E' + A_1' = E'$). This particular combination band has been found to be strong in other infrared spectra and some force constant calculations to be presented later predict the A_1' species near 800 cm^{-1}. The assignment of this combination band is well justified by the above reasons and by the agreement of the observed and predicted isotopic shifts.

Nonplanar C_{3v} Symmetry Group.—The vibrational symmetry types for the C_{3v} group are $\Gamma_{vib} = 5\ A_1 + 2\ A_2 + 7\ E$, of which there are two completely inactive bands ($2\ A_2$) and twelve bands which are active in both the Raman and infrared ($5\ A_1 + 7\ E$). A correlation for the species between the D_{3h} and C_{3v} symmetry groups is presented in Table IV. It will be noted that there is no change in the number of nondegenerate or degenerate vibrations in going from one symmetry group to the other. This makes the assignments, based on the results already presented for D_{3h}, obvious. Five of the seven frequencies for the E species would correspond to the 5 E′ frequencies assigned in the D_{3h} case. This would leave two frequencies unobserved and presumably too weak or below our spectral cutoff at 250 cm^{-1}. Only one of the frequencies for the A_1 species could be assigned corresponding to the A_2'' vibration at 918 cm^{-1}. Two of the A_1 species could easily be hidden by the asymmetric vibrations at 2620 and 1389 cm^{-1}. All the assignments made for the C_{3v} symmetry group including those for the combination and overtone bands are summarized in Table I.

TABLE IV[19]

CORRELATION TABLE FOR $D_{3h} \rightarrow C_{3v} \rightarrow C_{2v} \rightarrow C_s$

D_{3h}	C_{3v}	C_{2v}	C_s
A_1'	A_1	A_1	A'
A_2'	A_2	B_2	A''
E'	E	$A_1 + B_2$	$A' + A''$
A_1''	A_2	A_2	A''
A_2''	A_1	B_1	A'
E''	E	$A_2 + B_1$	$A' + A''$

Discussion

Raman spectra of boroxine could not be obtained because of its instability, but for the somewhat similar molecule (borazine) Raman spectra are known and much better (higher pressure) infrared spectra have been obtained, so that more information is available for an analysis of the vibrational motion of the molecule. Because of the similarities of the infrared spectra of borazine and boroxine, it was thought that one could use the borazine results in order to complete the analysis of boroxine. The similarities extend to both spectra showing a double Q branch around 918 cm^{-1} for the spectra containing the natural abundances of boron-10 and -11 which upon deuteration of the molecule shifts to around 800 cm^{-1} and shows multiple Q branches (compare Figure 3 with the spectra found either in ref 16 or 17). The reason for the multiple Q branches in borazine has not been determined; however, for both boroxine and borazine it seems reasonable to conclude that these bands are due to the many isotopic species possible in the partially deuterated molecules. One would like to be able to explain the origin of these bands from the corresponding vibrations in the completely symmetric molecule (*i.e.*, $H_3B_3O_3$). In the case of boroxine, it seems that the complexity of the 800-cm^{-1} region in the partially deuterated molecules is not due to a shift of the frequency corresponding to the A_2'' vibration in the hydrogen molecule, for a glance at Table III shows that the shift in the partially deuterated molecules would have to be greater than in the $D_3B_3O_3$ molecule, which does not seem too likely. For the D_{3h} symmetry group, if one assumes that there is an E″ vibration near the assigned A_2'' vibration at 918 cm^{-1} (both out-of-plane BH motions), then the multiple Q branches in the spectra of the partially deuterated molecules could be due to a shift of both of these bands into the 800-cm^{-1} region, where the E″ would go over into the infrared-active B_1 vibration. This assumption would require that an inactive vibration (E″) in the completely symmetric molecule become quite strongly active in the partially deuterated molecules. The complexity can be more easily explained by assuming a nonplanar C_{3v} molecule. In this case the two vibrations (A_1 and E) which would shift into the 800-cm^{-1} region would both be infrared active in all of the isotopic species (*i.e.*, $D_3B_3O_3$ or the partially deuterated molecules), and, therefore, only an increase in intensity of the bands would be required.

In the spectrum of the completely deuterated molecule (Figure 2) a band appearing as a Q branch was observed at 783 cm^{-1}. Experiments indicated that this band was not due to the partially deuterated species. One possible explanation for the complexity of the band around 800 cm^{-1} and in particular the Q branch at 783 cm^{-1} is the presence of hot bands in the spectrum. If one assumes that the lowest frequency vibration for boroxine is around 300 cm^{-1} by analogy with the assigned E″ vibration in borazine, a Boltzmann distribution calculation shows that approximately 25% of the molecules would be in this vibrational state. The problem with this assumption is suggesting appropriate upper levels for a transition in the 800-cm^{-1} region.

In borazine a band at 394 cm^{-1} has been assigned to an out-of-plane ring vibration (A_2'') by various authors;[16,17] the corresponding band in boroxine has not been observed, although a search down to 250 cm^{-1} was made. It was expected that the band in boroxine might occur at a lower frequency, because of the heavier oxygen atoms in the ring and the possibility of a weaker force constant for the out-of-plane motion.

It is not possible on the basis of the infrared spectrum alone to conclude whether the boroxine molecule is planar or nonplanar. Arguments for the planar D_{3h} molecule would include the good agreement for the product rule calculation of the in-plane E′ vibrations and the analogy with the spectrum of borazine, which would require that there be no question about the planarity of borazine. However, if the boroxine molecule is only slightly nonplanar, it would be expected that the theoretical results of the E′ product rule calculation would agree for five of the seven E-type vibrations. Therefore, the product rule calculations for D_{3h} symmetry group would not rule out the possibility of a slightly nonplanar C_{3v} molecule. One of the major arguments in favor of the nonplanar C_{3v} molecule is the explanation of the complex band in the 800-cm^{-1} region of the spectrum for the partially deuterated molecules.

Force Constant Calculations

It would appear that, because of the good agreement found for the product rule calculations on the E′ vibrations in the D_{3h} symmetry group, the molecule must be planar or very nearly so. In order to gain more information about the vibrations of the boroxine molecule, including unobserved frequencies and normal coordinates, a normal-coordinate analysis was undertaken. If the boroxine molecule is nonplanar and has C_{3v} symmetry, it would be expected that the degree of nonplanarity would be small. Thus, a force constant calculation based upon the assumption of a planar molecule with D_{3h} symmetry would give results which would be very close to those expected for the nonplanar C_{3v} model.

The D_{3h} model chosen for the calculations had the following parameters. The BH and BO distances were taken as 1.181 and 1.38 Å, respectively, based upon the distances found from a microwave study on the $H_2B_2O_3$ molecule.[23] Because there is evidence that $C_3N_3H_3$, $B_3O_3(OH)_3$ and $B_3O_3(CH_3)_3$ are not regular hexagonal,[24-26] the OBO and BOB angles were taken as 126 and 114°, respectively, instead of the more usual OBO = BOB = 120°.

The program used for the adjustment of the vibrational force constants is based upon the papers of Overend and Scherer,[27,28] and Mann, Shimanouchi, Meal, and Fano.[29] The details of the method used for the refinement of the force constants by least squares is very nicely summarized in an article by Schachtschneider and Snyder.[30] Only a fraction (0.25) of the computed correction was applied to ensure convergence upon a solution.[27,29] The distribution of the potential energy among the various force constants (f) was obtained by applying the method of Morino and Kuchitsu.[31] The actual details of the program are standard and do not require comment here.

Using a simple valence force field with one interaction constant, the potential energy for the in-plane motion had the form

$$2V = \sum_{i=1}^{3} (f_s)s_i^2 + \sum_{i=1}^{6} (f_t)t_i^2 + \sum_{i=1}^{3} (f_\alpha)(t_0\alpha_i)^2 + \sum_{i=1}^{3} (f_\beta)(t_0\beta_i)^2 + \sum_{i=1}^{3} (f_\xi)(s_0\xi_i)^2 + 2\sum_{i=1}^{6} (f_{t\xi})t_0t_i\xi_i$$

where $s_0 = 1.181$ and $t_0 = 1.38$ Å and the internal coordinates, s, t, β, and φ, are shown in Figure 4. Rather than use the less physically meaningful force constant associated with φ, it was decided to use the linear combination of φ

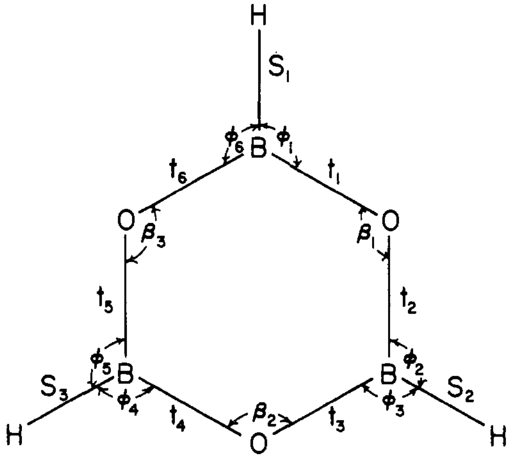

Figure 4.—In-plane internal coordinates for boroxine.

$$\alpha_1 = \varphi_6 + \varphi_1 \qquad \xi_1 = \varphi_6 - \varphi_1$$
$$\alpha_2 = \varphi_2 + \varphi_3 \qquad \xi_2 = \varphi_2 - \varphi_3$$
$$\alpha_3 = \varphi_4 + \varphi_5 \qquad \xi_3 = \varphi_4 - \varphi_5$$

In this way we could use the constants f_α and f_ξ, which are associated with the ring bending and the BH bending motions, respectively. Counting the degenerate vibrations as two frequencies, there are 15 in-plane frequencies, for which we have 18 internal coordinates. This gives us three redundant coordinates and, therefore, three zero roots in the secular equation. Since the program would have no trouble with the zero roots, it was decided to leave the redundancies as a check on the correctness of the calculations. It was found that owing to the high correlation of the constants f_α and f_β it was necessary to assume that $f_\alpha = f_\beta$. Preliminary calculations indicated that in order to obtain a good fit (less than 10% error) for the frequencies at 1389 and 990 cm^{-1} it was necessary to include the interaction constant $f_{t\xi}$. Using the three isotopic species, $H_3{}^{11}B_3{}^{16}O_3$, $H_3{}^{10}B_3{}^{16}O_3$, and $D_3{}^{11}B_2{}^{16}O_3$, the damped least-squares program converged upon the values of the force constants listed in Table V. The frequencies for the other two isotopic species, $H_3{}^{11}B_3{}^{18}O_3$ and $D_3{}^{11}B_3{}^{18}O_3$, were then calculated and compared with those

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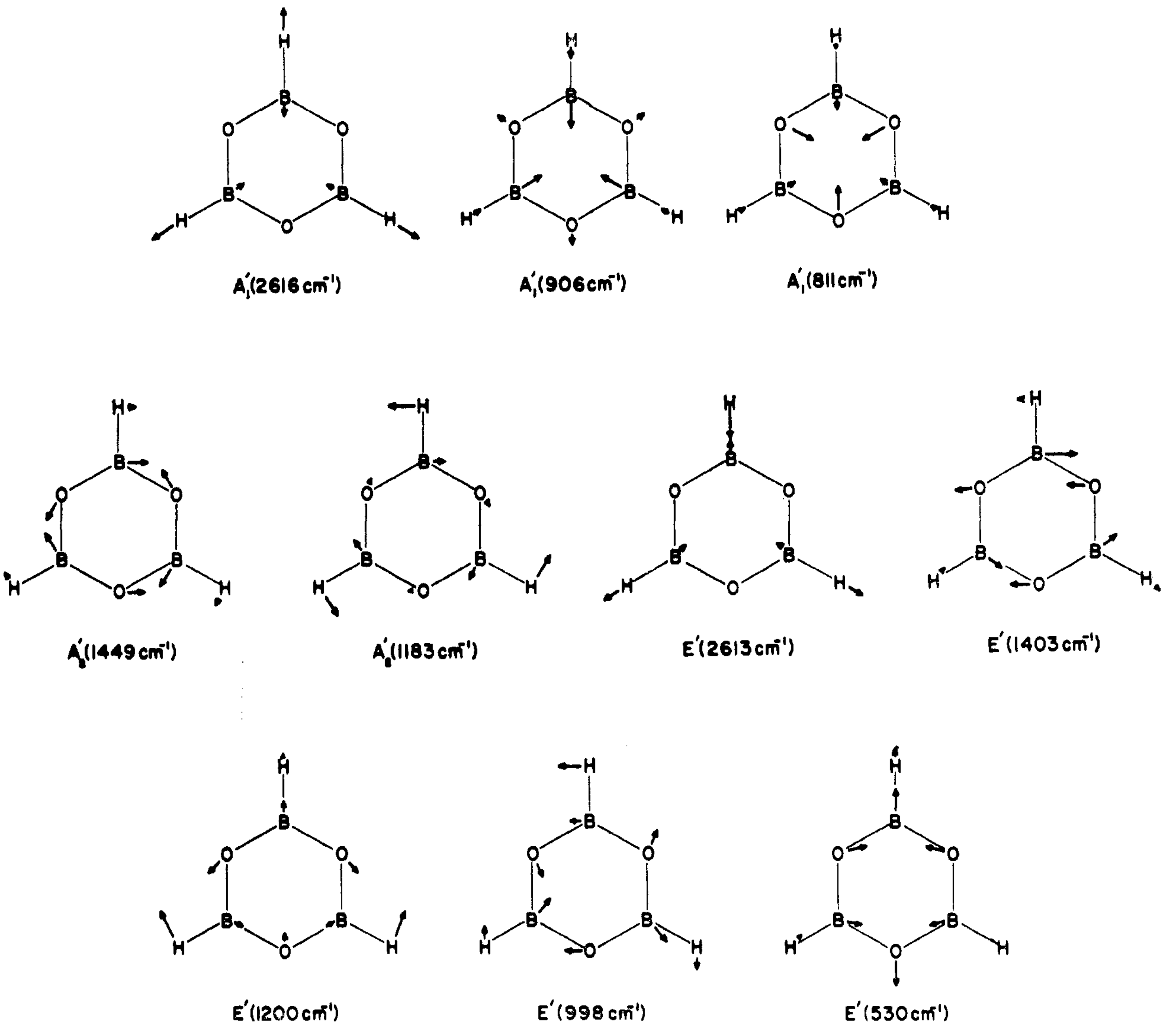

Figure 5.—Normal vibrations for the in-plane vibrations of $H_3{}^{11}B_3{}^{16}O_3$ (frequencies in parentheses are those obtained from force constant calculations).

observed as an independent check on the calculated force constants. The errors listed in Table V for the various force constants are based upon the least-squares fit and are not necessarily an estimate of the true uncertainty of the force constants. The force constants were not strongly correlated, the largest correlation coefficient being $\rho(f_t, f_{t\xi}) = -0.67$. The frequencies calculated from these force constants (Table V) are shown in Table VI along with the observed frequencies. Except for a few vibrational frequencies in the deuterated molecules, the percentage error between the calculated and observed frequencies was less than 3%. The largest percentage error was 6.6%. The normal vibrations as calculated for the $H_3{}^{11}B_3{}^{16}O_3$ molecule are shown in Figure 5; only one of the E′ vibrations for each degenerate level is shown. Because of the interaction constant, the method of Morino and Kuchitsu for calculating the potential energy distribution among the various force constants gives negative percentages. Still the results, as shown in Table VII for $H_3{}^{11}B_3{}^{16}O_3$ are qualitatively meaningful

TABLE V

CALCULATED FORCE CONSTANTS

Type	Symbol	Value[a]
BH stretching	f_s	3.68 ± 0.05
BO stretching	f_t	5.64 ± 0.09
Ring bending	$f_\alpha = f_\beta$	0.58 ± 0.01
BH in-plane bending	f_ξ	0.65 ± 0.01
BO stretching–BH bending, interaction constant	$f_{t\xi}$	−0.38 ± 0.03

[a] mdyn/Å.

TABLE VI

OBSERVED AND CALCULATED VIBRATIONAL FREQUENCIES (CM^{-1})

Symmetry type	$H_3{}^{11}B_3{}^{16}O_3$		$H_3{}^{10}B_3{}^{16}O_3$		$D_3{}^{11}B_3{}^{16}O_3$		$H_3{}^{11}B_3{}^{18}O_3$		$D_3{}^{11}B_3{}^{18}O_3$	
(D_{3h})	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
A_1'	2616	...	2630	...	1959	...	2616	...	1959	...
A_1'	906	...	941	...	865	...	902	...	855	...
A_1'	811	...	814	...	803	...	768	...	765	...
A_2'	1448	...	1487	...	1440	...	1414	...	1407	...
A_2'	1183	...	1190	...	886	...	1182	...	881	...
E′	2613	2620	2627	2624	1954	1948	2613	2610	1953	1940
E′	1403	1389	1448	1428	1395	1373	1377	1365	1369	1340
E′	1200	1213	1206	1228	1065	1133	1186	1185	1033	1107
E′	998	990	1015	1025	785	760	981	975	784	758
E′	530	530	539	537	520	520	512	508	503	503

TABLE VII

POTENTIAL ENERGY DISTRIBUTION (%) FOR $H_3{}^{11}B_3{}^{16}O_3$

Symmetry (D_{3h})	Calcd freq, cm^{-1}	Force constants				
		f_s	f_t	$f_\alpha = f_\beta$	f_ξ	$f_{t\xi}$
A_1'	2616	98.6	0.6	0.8	0.0	0.0
A_1'	906	1.3	13.2	85.5	0.0	0.0
A_1'	811	0.1	86.2	13.7	0.0	0.0
A_2'	1448	0.0	100.9	0.0	0.0	−1.0
A_2'	1183	0.0	7.5	0.0	108.4	−16.0
E'	2613	98.8	0.7	0.5	0.0	0.0
E'	1403	0.3	94.4	11.6	11.4	−17.6
E'	1200	0.2	22.1	2.7	79.6	−4.6
E'	998	0.6	67.4	8.6	16.2	7.2
E'	530	0.1	14.9	85.5	1.1	−1.6

for showing which force constants are most instrumental for determining the vibrational frequencies.

Because of the many isotopic species of boroxine which can be prepared, it would be possible to extend these calculations by including many more interaction constants. Until a more detailed knowledge of the structure is obtained, a detailed calculation would not be any more meaningful than the one presented. Except for the large negative interaction constant the values for the other constants seem to be quite reasonable. The large negative interaction constant may be necessary because of the polarity of the bonds in boroxine and/or because of the use of an incorrect model (D_{3h} symmetry, bond lengths, etc.). The value for the BH stretching constant is only slightly higher than those reported for borazine. A comparison of the other constants with borazine will have to await a calculation for the borazine molecule based upon the new vibrational assignments being reported in the literature.[16,17]

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Bis-Amine Derivatives of $BH_2{}^+$ with Methylpyridines

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Boron cations, $H_2B(amine)_2{}^+$, with a number of different methylpyridines, have been synthesized through three different routes: (1) from sodium borohydride, iodine, and various amines; (2) from trimethylamine borane, iodine, and amines; (3) from trimethylamine monoiodoborane and different amines. The third method, involving heating of trimethylamine monoiodoborane with excess of the appropriate amine, is found to be the most convenient one and it gives high yields. The boronium[1] salts were quite stable and were characterized by analysis of the hexafluorophosphates and by their uv, ir, and nmr spectra.

Introduction

A number of boronium salts and their properties have been prepared by Muetterties[2,3] and Douglass,[4] and a study of the synthesis and formation kinetics of bis(pyridine)boronium ion has recently been published.[5] We now wish to report three apparently general synthetic methods to prepare bis(amine)boron cations, where two alkylpyridines are coordinated to a $BH_2{}^+$ group. The syntheses proceed from (1) borohydride salts, (2) trimethylamine borane, or (3) trimethylamine monoiodoborane, and give excellent yields of boron cations under mild conditions and from readily available starting materials. The third method is the most convenient and gives the highest yields with the least amounts of impurities or by-products. The general usefulness of these syntheses is illustrated by using methylpyridines and dimethylpyridines as examples.

Experimental Section

Materials.—Picolines and lutidines were obtained from Eastman Organic Chemicals and K & K Laboratories, Inc., respectively. The amines were distilled when necessary and dried and stored over Molecular Sieve 3A. Trimethylamine borane was used as obtained from Callery Chemicals Co. Sodium borohydride was supplied in good purity by Metal Hydrides, Inc. All other chemicals were reagent grade and were used without any further purifications, but were dried over Molecular Sieve when appropriate.

Synthesis of Bis(amine)boron Cations. (1). From Sodium Borohydride.[5]—Sodium borohydride (94% hydride purity), 0.793 g (19.7 mmol), was slurried in 24 ml of 4-picoline. Iodine solution, 7.290 g (29.0 mmol) in 190 ml of benzene, was added very slowly while the picoline–borohydride slurry was stirred. During the addition of iodine, hydrogen gas was evolved, and in the early stages, the reaction was very fast. The solution was heated gradually to 70°, and the addition of iodide was continued. When all the iodine had been added, a permanent iodine color developed, and, on further heating for 1 hr, the color still persisted. The amounts of iodine used corresponded closely to the quantities calculated according to

$$2NaBH_4 + 6C_6H_7N + 3I_2 \longrightarrow 2\ NaI + H_2 + 2(C_6H_7N)_2BH_2{}^+I^- + 2C_6H_7NH^+I^-$$

The reaction mixture was evaporated to dryness under vacuum, and the resulting solid mixture was extracted with 100 ml of dry chloroform and filtered. The leftover solid, after washing with

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[1] In accord with past usage, the term boronium is used here to designate a boron cation. The Nomenclature Committee of the American Chemical Society recommends the term bis(amine)dihydroboron(H).

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