# Matrix Isolation Study of the Reactions of $B_2H_6$ with Pyridine, Pyrrole, and Pyrrolidine: Spectroscopic Characterization of $C_4H_9N \cdot BH_3$ and $C_4H_8N = BH_2$

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The products of the pyrolytic reaction of  $B_2H_6$  with pyrrole, pyrrolidine, and pyridine have been isolated in argon matrices at 14 K and characterized by infrared spectroscopy. For the  $B_2H_6/C_4H_9N$  system, complex formation was observed at temperatures between ambient and 200 °C and the subsequent H<sub>2</sub> elimination product H<sub>2</sub>B=NC<sub>4</sub>H<sub>8</sub> at pyrolysis temperatures above 50 °C. The B=N stretching frequency (1486 cm<sup>-1</sup>) and local density functional calculations done in support of the experiments both support substantial double-bond character for the boron-nitrogen bond. The reaction of B<sub>2</sub>H<sub>6</sub> with pyridine led to formation of the H<sub>3</sub>B·NC<sub>5</sub>H<sub>5</sub> complex only, while copyrolysis of B<sub>2</sub>H<sub>6</sub> with pyrrole led to no reaction even when a pyrolysis temperature of 380 °C was employed. This result is best understood in terms of the role of the nitrogen lone pair in the aromaticity of the pyrrole ring.

#### Introduction

Diborane,  $B_2H_6$ , has long been of interest to chemists as a consequence of its unusual bonding and electron-deficient nature.<sup>1-3</sup>  $B_2H_6$  is known to react with a variety of Lewis bases, forming both covalent and ionic compounds as a function of reaction conditions.<sup>4.5</sup> High-temperature gas-phase reactions of  $B_2H_6$  with Lewis bases have been studied extensively in this laboratory in recent years, followed by the trapping of product species into low-temperature matrices. These studies<sup>6-10</sup> have resulted in the identification and infrared spectroscopic characterization of many reactive boron intermediates, including  $H_2B=NH_2$ ,  $H_2B=OCH_3$ , and  $H_2B=SH$ .

Pyrrole ( $C_4H_5N$ ), pyrrolidine ( $C_4H_9N$ ), and pyridine ( $C_5H_5N$ ) are representative members of the class of cyclic amines; pyrrole and pyrrolidine are five-membered rings with an active hydrogen on the nitrogen atom, while pyridine is a six-membered ring without an active hydrogen on the nitrogen atom. Previous studies have suggested formation of an initial adduct of the base with BH<sub>3</sub>, followed by H<sub>2</sub> elimination from bases containing an active hydrogen.<sup>6-10</sup> Similar reactions might well be anticipated here, leading to similar complexes and (in the cases of pyrrole and pyrrolidine) the analogous H<sub>2</sub> elimination products. Such observations would lend additional support to the reaction mechanism proposed earlier.

The matrix isolation technique<sup>11-13</sup> was developed for the study of reactive intermediates, both neutral and charged, after isolation in an inert solid at cryogenic temperatures. The merged jet copyrolysis technique has proven to be an effective means of producing reactive boron intermediates.<sup>6</sup> In view of the interest in these systems, a study was undertaken to examine the products formed following merged jet copyrolysis of diborane with pyrrole, pyrrolidine, and pyridine.

## **Experimental Section**

All of the experiments in this study were carried out on conventional equipment that has been described.<sup>14</sup> The merged jet copyrolysis apparatus has also been outlined.<sup>6</sup> Pyrrole (Aldrich), pyrrolidine, and pyridine (both MCB) were all introduced into the vacuum line as the vapor above the liquid after purification by repeated freeze-pump-thaw cycles at 77 K. The cyclic amines adsorbed strongly to the wall of the metalvacuum system, making accurate determination of sample concentration difficult. Based on experimental procedures and observed band intensities, sample concentration ratios Ar/amine were estimated to be between 500/1 and 1000/1. B<sub>2</sub>H<sub>6</sub> (Matheson) was introduced into the vacuum line as a 1% mixture in argon and then further diluted with argon to the desired ratio. Each sample was then deposited via the merged jet codeposition technique onto a 14 K cold window for 12–24 h before final scans were recorded on a Nicolet IR 42 Fourier transform infrared spectrometer at 1-cm<sup>-1</sup> resolution. Pyrolysis temperatures as high as 360 °C were employed.

To provide theoretical support for the experimental spectra, structures and vibrational spectra were calculated using local density functional (LDF) methods. The program DMOL (Biosym Technologies) was employed on a Silicon Graphics Personal Iris workstation. The calculations led to an optimized geometry and unscaled vibrational frequencies.

## Results

Before any copyrolysis experiments were conducted, blank experiments involving argon and the different cyclic amines were carried out both at room temperature and with the deposition line at elevated temperatures. The spectra were in good agreement with literature spectra.<sup>15-19</sup>

 $B_2H_6 + C_4H_9N$ . When a sample of Ar/B<sub>2</sub>H<sub>6</sub> = 1000 was allowed to flow with a sample of Ar/C<sub>4</sub>H<sub>9</sub>N through the merged jet apparatus, with the deposition line at room temperature, an extensive set of new infrared absorptions was noted, as listed in Table I. Certain of these bands at 1097, 1182, 1188, 2293, 2330, 2382, and 2405 cm<sup>-1</sup> were somewhat broad compared to most bands of matrix isolated species. These bands were reproducible as sample concentrations were varied.

When mild heating of the pyrolysis zone was carried out to temperatures of 40 and 100 °C, these bands were seen to intensify. In addition, new bands at 722, 910, 943, 970, 1083, 1092, 1161 (br), 1209, 1486, 1507, 2553, 2860, 2983, and 3342 cm<sup>-1</sup> were observed. Some of these are also listed in Table I, while some are listed in Table II. When the pyrolysis zone was heated to 200 °C, bands listed in Table I decreased slightly in intensity, while those in Table II were slightly more intense. When the pyrolysis zone was heated to 350 °C in a subsequent experiment, all of the bands listed in Table I were absent from the spectrum. In contrast, the bands listed in Table II intensified. These results are shown in Figure 1 for the B–H stretching region. The most intense

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TABLE I: Band Positions (in cm<sup>-1</sup>) and Assignments for Matrix-Isolated H<sub>2</sub>B·N(H)C<sub>2</sub>H<sub>2</sub>

LE	II:	Band	<b>Positions</b>	(in	cm <sup>-1</sup> )	and	Assignments	for	
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**TABLE II:** 

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Ar matrix	DMOL	% diff	assignment
2247	2212		N_H otr
3342	3312	0.9	C H str
3170	3034	4.5	C-H su
2007	3024	0.2	C-H str
3007	3017	0.3	
3000	3000	0.0	C-H sti
2992	2977	0.5	C-H str
2983	2909	0.3	C-H str
2900	2930	0.0	C-H str
2890	2943	1.0	DLL of (10P)
2417	2420	1.0	$\mathbf{D}\mathbf{H}_{3}$ str (11 $\mathbf{P}$ )
2403 (Br)	2429	1.0	DII sta (10D)
2370	2419	15	BU, str (11B)
2302 2202 (hr)	2410	20	BH <sub>3</sub> str (llB)
2293 (DF)	2300	4.9	
1409	1404	0.5	
1403	1439	1.0	
1204	1430	1.0	
1394	1409	1.0	$CH_4 \pm N$ H hand
1304	1336	1.5	
1320	1300	1.5	$CH_4 \pm N$ U head
1310	1200	2.1	$CH_2^{-}$ + N-H benu
1240	1203	0.6	
1240	1233	0.0	
1227	1205	1.5	$CH_4 \perp N_{-}H$ hend
1209 1199 (ha)	1190	1.1	$PU_1 def(10R)$
1100 (DF)	1142	3.4	BU, def (llB)
1162 (01)	1142	3.4	
1161	1133	20	BH. def (llB)
1101	1127	2.9	BH3 def
1150	1104	4.0	BH, def (11B)
1007 (br)	1080	1.5	$\mathbf{B}_{\mathbf{N}}$ str ( <sup>11</sup> $\mathbf{B}$ )
1097(01) 1092(br)	1000	1.5	$\mathbf{D}$ = 14 still ( $\mathbf{D}$ )
1092 (01)	1033	4.6	CH.4
1049	1000	4.6	$CH_{a}^{a}$ + ring <sup>b</sup>
043	969	2.8	ringb
745	950	2.0	$ringb + BH_{2}$
927 (br)	935	0.9	$BH_{2} def (^{11}B)$
923	914	10	$CH_{2}^{a}$
910	884	29	$ring^{b} + BH_{2}$
892	856	4.0	$ring^b + BH_2$
	813		$ring^b + BH_3$
750	789	5.2	ring <sup>b</sup>
701	712	1.6	ring <sup>b</sup>
686	574°	16.3	ring <sup>b</sup>

<sup>a</sup> CH<sub>2</sub> rocking, bending, and twisting modes. <sup>b</sup> Skeletal vibrations of the ring. <sup>c</sup> Four additional modes were calculated at low energy (204, 363, 263, and 204 cm<sup>-1</sup>) but not observed.

absorption in Table II, at 1486 cm<sup>-1</sup>, was over 2 absorbance units (see Figure 2). In a series of additional experiments, conditions of concentration and pyrolysis temperature were varied systematically, and intensity changes were noted for the different product absorptions. These results are also illustrated in the survey scans of Figures 3 and 4.

 $B_2H_6 + C_5H_5N$ . When a sample of  $Ar/B_2H_6$  was codeposited with a sample of  $Ar/C_5H_5N$  through the merged jet deposition system, a number of new infrared absorptions were seen that could not be attributed to either parent species. These are listed in Table III. When the pyrolysis zone was heated stepwise from room temperature to 360 °C in a series of experiments, the bands listed in Table III were seen to decrease in intensity. When the pyrolysis temperature was 260 °C, these product bands were completely absent, and no new absorptions were observed. Bands due to the parent species were observed throughout. The same result was obtained at a pyrolysis temperature of 360 °C.

 $B_2H_6 + C_4H_5N$ . When these two compounds, each diluted in argon, were codeposited through the room temperature merged jet apparatus for 24 h, no new infrared absorptions were seen in the resultant spectrum. When the pyrolysis zone was heated in a stepwise fashion to as high as 360 °C in a series of experiments, again no new absorptions were seen. Parent bands of pyrrole

Ar matrix	DMOL	% diff	assignment
2002	2014	0.7	C H ata
2992	2000	0.7	
2085	2777	0.1	C-H str
2903	2901	0.1	C-H str
2370	2972	0.2	C-H str
	2961		C-H str
	2958		C-H str
2860	2938	27	C-H str
2568	2750	2.7	BH <sub>2</sub> antisym str ( <sup>10</sup> B)
2553	2575	0.9	$BH_2$ antisym str ( <sup>11</sup> B)
2490 (br)	2490	0.0	$BH_2$ sym st ( <sup>11</sup> B)
1507		••••	$B = N \operatorname{str}({}^{10}B)$
1486	1461	1.7	$\mathbf{B} = \mathbf{N} \operatorname{str} (^{11}\mathbf{B})$
1471	1465	0.4	CH <sub>2</sub> <sup>a</sup>
1463	1446	1.2	CH <sub>2</sub> <sup>a</sup>
1452	1422	2.1	CH <sub>2</sub> <sup>a</sup>
1449	1412	2.6	CH <sub>2</sub> <sup>a</sup>
1342	1311	2.3	CH <sub>2</sub> <sup>a</sup>
1294	1305	0.9	CH <sub>2</sub> <sup>a</sup>
1287	1258	2.2	CH <sub>2</sub> <sup>a</sup>
1234	1224	0.8	$CH_2^a$
1229	1222	0.6	$CH_{2^{a}}$
1209	1215	0.5	CH <sub>2</sub> <sup>a</sup>
11 <b>97</b>	11 <b>94</b>	0.3	$CH_2^{a} + ring^{b}$
	1173		$CH_2^a + ring^b$
1174			$BH_2$ sym bend ( <sup>10</sup> B)
1167	1136	2.6	$BH_2$ sym bend ( <sup>11</sup> B)
1155	1091	5.5	CH <sub>2</sub> <sup>a</sup>
	1088		$CH_{2^{a}} + ring^{b}$
1048	1009	3.7	$CH_{2}^{a} + ring^{b}$
1017	993	2.4	$CH_{2^{a}} + ring^{b}$
988			BH <sub>2</sub> out-of-plane ( <sup>10</sup> B)
983	918	6.7	$BH_2$ out-of-plane ( <sup>11</sup> B)
976			$BH_2$ rock ( <sup>10</sup> B)
972	933	4.0	ring <sup>b</sup> + BH <sub>2</sub> out-of-plane
970	861	11.2	$BH_2 \operatorname{rock} (^{11}B)$
955	910	4.7	ring <sup>b</sup> + BH <sub>2</sub> out-of-plane
	783		CH <sub>2</sub> <sup>a</sup>
	749		$CH_2^a + ring^b$
722	725	0.4	CH <sub>2</sub> <sup>a</sup>
	675		ring <sup>o</sup>
	605		ring <sup>o</sup>
	500°		BH <sub>2</sub> twist

<sup>a</sup> CH<sub>2</sub> rocking, bending, and twisting modes. <sup>b</sup> Skeletal modes of the ring. <sup>c</sup> Four additional modes were calculated t lie below 400 cm<sup>-1</sup> but were not observed.



Figure 1. Infrared spectra, between 2250 and 2650 cm<sup>-1</sup>, of the products formed through the merged jet copyrolysis of samples of  $Ar/B_2H_6$  and  $Ar/C_4H_9N$  and trapping into an argon matrix at 14 K. The upper trace shows the spectrum of the products following pyrolysis at 350 °C, while the lower trace shows the spectrum of the products following pyrolysis at 200 °C.

were quite intense, while parent bands of  $B_2H_6$  were diminished at high temperatures, as has been seen previously.6-10

## Discussion

Product Identification. The copyrolysis of samples of Ar/  $B_2H_6$  with  $Ar/C_4H_9N$  and  $C_5H_5N$  led to many distinct new



Figure 2. Infrared spectrum, between 1350 and 1550 cm<sup>-1</sup>, of the products arising from the merged jet copyrolysis of samples of  $Ar/B_2H_6$  and  $Ar/C_4H_9N$  at 350 °C followed by deposition onto a 14 K cold surface.



Figure 3. Infrared spectrum, between 600 and 3400 cm<sup>-1</sup>, of the products arising from the merged jet copyrolysis of samples of  $Ar/B_2H_6$  and  $Ar/C_4H_9N$  at 350 °C followed by deposition onto a 14 K cold surface.



Figure 4. Infrared spectrum, between 400 and 3400 cm<sup>-1</sup>, of the products arising from the ambient temperature merged jet deposition of samples of  $Ar/B_2H_6$  and  $Ar/C_4H_9N$  onto a 14 K cold surface.

infrared absorptions that could not be attributed to either parent species, while copyrolysis of samples of  $Ar/B_2H_6$  with samples of  $Ar/C_4H_5N$  led to no new infrared absorptions. (The differences in these systems will be discussed below.) For the two systems where reaction did occur, a number of experiments were conducted over a range of pyrolysis temperatures and sample concentrations. Intensity variations of the product absorptions as a function of experimental conditions were used to determine the number of product species for each system.

For the  $B_2H_6/C_3H_5N$  system, all of the product absorptions maintained a constant intensity ratio with respect to one another over the full range of temperature and concentration conditions employed. This indicates that only a single product absorber is being formed in these experiments. Moreover, as seen in Table III, these product absorptions match very closely the spectrum<sup>20</sup> reported for the well-known adduct H<sub>3</sub>B·NC<sub>5</sub>H<sub>5</sub>. This result is also consistent with an earlier study<sup>7</sup> of the reaction of B<sub>2</sub>H<sub>6</sub> with amines, where BH<sub>3</sub> adduct formation was observed when the amine did not contain an active hydrogen (hydrogen bonded to the nitrogen atom). On this basis, the product species in the B<sub>2</sub>H<sub>6</sub>/C<sub>5</sub>H<sub>5</sub>N system is identified as the H<sub>3</sub>B·NC<sub>5</sub>H<sub>5</sub> complex.

TABLE III: Band Positions (in cm<sup>-1</sup>) and Assignments for Matrix-Isolated  $H_3B\cdot NC_5H_5$ 

Ar matrix	literature <sup>a</sup>	assignment
3128		C-H str <sup>b</sup>
3088		C-H str <sup>b</sup>
3067		C–H str <sup>b</sup>
3021	3010	C–H str <sup>b</sup>
2419 (br)		BH3 antisym str
2387	2350	BH3 antisym str
2298	2280	BH <sub>3</sub> sym str
1623	1624	C-C str + C-N str
1586	1580	C-C str + $C-N$ str
1488	1488	C-H bend <sup>b</sup>
1461	1459	C-H bend <sup>b</sup>
1344		C-H rock <sup>b</sup>
1250		C-H rock <sup>b</sup>
1182 (br)	1168	BH <sub>3</sub> def
1176		site splitting
1161		C-H rock <sup>b</sup>
1088 (br)		<b>B–N str</b> ( <sup>10</sup> <b>B</b> )
1082	1090	$B-N \operatorname{str}(^{11}B)$
1022	1020	C-H rock <sup>b</sup>
964		ring mode
933		$BH_3 def (^{10}B)$
925 (br)	920	$BH_3 def(^{11}B)$
922		site spliting
751		C-H wag
686		C–H wag

<sup>a</sup> From ref 20. <sup>b</sup> Assignment by analogy to parent C<sub>5</sub>H<sub>5</sub>N.

For the  $B_2H_6/C_4H_9N$  system, the variation of product band intensities with differing pyrolysis temperatures indicated that two separate and distinct absorbers could be identified. The first set of absorptions, listed in Table I, were found to maintain a constant intensity ratio with respect to one another and must be assigned to a single absorber. Several absorptions can be readily identified as <sup>10</sup>B, <sup>11</sup>B isotopic doublets on the basis of splittings and intensities. (Boron occurs in nature in a 20:80 ratio, <sup>10</sup>B: <sup>11</sup>B.) This indicates the presence of boron in the absorbing species. Bands associated with this species were clearly noted in the BH<sub>3</sub> stretching region (2250-2400 cm<sup>-1</sup>) and not in the terminal BH<sub>2</sub> stretching region (2400-2600 cm<sup>-1</sup>). Several broad bands were noted in the BH<sub>3</sub> deformation region, and a single new absorption was seen in the N-H stretching region (above  $3300 \text{ cm}^{-1}$ ). Several additional bands in the C-H stretching and bending regions were noted as well. These results point to the formation of the adduct  $H_3B \cdot NC_4H_9$ , analogous to the  $H_3B \cdot NC_5H_5$  adduct reported above. While the latter adduct has been reported previously the former, pyrrolidinoborane, has not been seen and characterized previously. As such, this represents the first identification of this compound.

The second set of bands from the  $B_2H_6/C_4H_9N$  system, listed in Table II, maintained constant intensity ratios with respect to one another, but not with respect to the bands in Table I. Thus, these absorptions must be assigned to a single new absorber. Again, several doublets were noted with splittings and band intensities indicative of boron incorporation. In this case, bands were noted in the BH<sub>2</sub> stretching region rather than in the BH<sub>3</sub> stretching region. Also, a very intense doublet was noted at 1486, 1506 cm<sup>-1</sup> in the B=N stretching region while no absorptions were seen for this absorber in the N-H stretching region. Finally, the product responsible for this set of absorptions was only formed at temperatures above 50 °C with a yield that increased with temperature up to 350 °C. Similar H<sub>2</sub> elimination products (e.g., H<sub>2</sub>B=NH<sub>2</sub>, H<sub>2</sub>B=OCH<sub>3</sub>, and H<sub>2</sub>BSH) were formed, after observation of the 1:1 adduct. All of this information leads to the assignment of the set of bands listed in Table II to the  $H_2$ elimination product pyrrolidinoborane,  $H_2B$ -NC<sub>4</sub> $H_8$ . While this compound was tentatively identified in two earlier synthetic studies,<sup>21,22</sup> the present study represents the first definitive identification and spectroscopic characterization of this species. DMOL calculations, band assignments, and the reaction mech-

TABLE IV: Calculated Geometry<sup>\*</sup> for H<sub>3</sub>B·N(H)C<sub>4</sub>H<sub>8</sub>

	$R_{B-N} = 1.59 \text{ Å} R_{B-H} = 1.20 \text{ Å}^{b} \alpha_{H-B-N} = 106^{\circ c} \alpha_{H-B-H} = 112^{\circ c} \alpha_{H-N-B} = 107^{\circ} \alpha_{H-N-C-C} = 170^{\circ d} \alpha_{B-N-C-C} = 170^{\circ d}$	
$R_{N-C} = 1.5 \text{ Å}^{e}$ $R_{C-C} = 1.5 \text{ Å}^{e}$ $R_{C-H} = 1.1 \text{ Å}^{b}$	Ring Geometry $\alpha_{N-C-C} = 105^{\circ c}$ $\alpha_{C-C-C} = 104.3^{\circ c}$	$\alpha_{\text{H-C-C}} = 112^{\circ f}$ $\alpha_{\text{H-C-H}} = 107^{\circ c}$

<sup>a</sup> Calculated by the local density functional program DMOL. <sup>b</sup> Equal bond lengths to  $\pm 0.01$  Å. <sup>c</sup> Equal bond angles to  $\pm 0.5^{\circ}$ . <sup>d</sup> Equal bond angles to  $\pm 1^{\circ}$ . <sup>e</sup> Equal bond lengths to  $\pm 0.03^{\circ}$ . <sup>f</sup> Equal bond angles to  $\pm 3^{\circ}$ .

TABLE V: Calculated Geometry<sup>a</sup> for H<sub>2</sub>B=NC<sub>4</sub>H<sub>8</sub>

$H_2B = NC_4$ skeleton is planar					
$R_{\rm B-N} = 1.38 {\rm \AA}$	$R_{\rm N-C} = 1.46$ Å	$\alpha_{N-C-C} = 107.5^{\circ d}$			
$R_{B-H} = 1.21 \text{ Å}^{b}$	$R_{C-C} = 1.53 \text{ Å}$	$\alpha_{C-C-C} = 106.8^{\circ d}$			
$\alpha_{\text{H-B-N}} = 119^{\circ c}$	$R_{C-H} = 1.10 \text{ Å}$	$\alpha_{\rm H-C-H} = 106^{\circ c}$			
$\alpha_{\text{H-B-H}} = 122^{\circ}$	$\alpha_{\mathbf{B}-\mathbf{N}-\mathbf{C}} = 124^{\circ c}$	$\alpha_{\text{H-C-C-H}} = 121^{\circ e}$			

<sup>a</sup> Calculated by the local density functional program DMOL. <sup>b</sup> Equal bond lengths to  $\pm 0.01$  Å. <sup>c</sup> Equal bond angles to  $\pm 0.5^{\circ}$ . <sup>d</sup> Equal bond angles to  $\pm 0.05^{\circ}$ . <sup>e</sup> For all trans hydrogens in the ring.

anism strongly support the assignment of these two sets of infrared absorptions (see below).

Local Density Functional Calculations. Local density functional (LDF) calculations using DMOL were performed on both  $H_3B$ - $NC_4H_9$  and  $H_2B$ = $NC_4H_8$  to provide assistance in the assigning of the observed infrared spectra. Both compounds optimized to stable geometries. The optimized structure of  $H_3B$ - $N_4H_9$  is presented in Table IV. The five-membered ring has an envelope shape with the four carbons nearly planar and the nitrogen "folded" out of the plane. This structure gives the hydrogen and the BH<sub>3</sub> group, each interacting with the nitrogen, a staggered conformation with respect to each other. This minimizes steric hindrance from the bulky ring.

The structure for  $H_2B$ =NC<sub>4</sub> $H_8$  is optimized to the geometry shown in Table V. This structure is planar along the  $H_2B$ =N ring skeleton (i.e., all atoms planar except the ring hydrogens). This is in accord with planar structures observed in the microwave spectra where boron is multiply bonded to nitrogen and oxygen<sup>23,24</sup> (e.g.,  $H_2B$ =NH<sub>2</sub> and  $H_2B$ =OCH<sub>3</sub>). A complete set of vibrational frequencies were calculated for each structure; these are listed and compared with the respective experimental frequencies in Tables I and II. The unscaled calculated frequencies were found to be in very good agreement with the observed frequencies, with only a few bands differing by more than 5% from the experimental value. The calculated frequencies assisted in the band assignments described below.

**Band Assignments.**  $H_2B = NC_4H_8$ . Pyrrolidinoborane is a 16atom molecule with 42 vibrational degrees of freedom. The symmetric planar geometry is in the  $C_{2\nu}$  point group. Vibrational modes belonging to the A<sub>1</sub>, B<sub>1</sub>, and B<sub>2</sub> irreducible representations are infrared-active and constitute the large majority of the vibrational frequencies for this molecule. This includes the B=Nstretch and all of the BH<sub>2</sub> motions except the BH<sub>2</sub> twist which is of  $A_2$  symmetry. However, the number of vibrations for this molecule and the similarity of motions of the ring and CH<sub>2</sub> units are such that complete assignment of all 42 normal modes is not possible with the spectra in hand. However, a number of key vibrations can be identified, compared to the LDF calculations, and used to characterize the product species. Even then, there is often extensive coupling between vibrational modes of similar frequency and the same symmetry, so that descriptions are necessarily approximate.

Two strong bands were observed at 2490 and 2553 cm<sup>-1</sup>; the

higher-energy band had a <sup>10</sup>B counterpart at 2568 cm<sup>-1</sup> while the 2490-cm<sup>-1</sup> band was sufficiently broad that a <sup>10</sup>B counterpart could not be resolved. These two absorptions are characteristic of a terminal BH<sub>2</sub> group. The BH<sub>2</sub> symmetric and antisymmetric stretches of H<sub>2</sub>B=NH<sub>2</sub> and a number of related compounds<sup>6-10</sup> have been seen within a few wavenumbers of these band positions. In addition, LDF calculations place the symmetric and antisymmetric stretching modes at 2490 and 2575 cm<sup>-1</sup>, respectively, very near the observed bands. Consequently, these two bands are so assigned.

A vibration of particular interest is the boron-nitrogen stretching frequency. An intense <sup>10</sup>B, <sup>11</sup>B doublet was observed at 1507, 1486 cm<sup>-1</sup> (see Figure 2). A boron isotopic shift of 21 cm<sup>-1</sup> is expected only for the vibration of the boron against a relatively heavy atom, in this case the nitrogen. For comparison, H<sub>2</sub>B=NH<sub>2</sub> exhibited a large 31-cm<sup>-1</sup> shift with the <sup>11</sup>B=N stretch coming at 1334 cm<sup>-1</sup>. LDF calculations placed the boron-nitrogen stretch at 1462 cm<sup>-1</sup>, in very good agreement with the observed position. The location of this band is strongly suggestive of doublebond character for the boron-nitrogen bond, as anticipated from earlier studies. The LDF calculations determined the B=N bond length to be 1.38 Å, very close to the experimental bond length<sup>23</sup> in  $H_2B$ =NH<sub>2</sub> of 1.40 Å and the C=C bond length in ethene<sup>25</sup> of 1.35 Å. (The bond length of the C-C bond in ethane is 1.57 Å.) All of this points to assignment of 1486-cm<sup>-1</sup> to the B=Nstretch and indicates that the boron-nitrogen bond has substantial double-bond character.

Several additional <sup>10</sup>B, <sup>11</sup>B doublets were observed at lower energy, at 970, 976 cm<sup>-1</sup>, 983, 988 cm<sup>-1</sup>, and 1167, 1174 cm<sup>-1</sup>. These are in the region of the BH<sub>2</sub> rocking, out-of-plane wagging, and symmetric bending modes. Based on comparison to spectra of similar compounds and the LDF calculations for these modes, the assignments indicated in Table II are made. It should be noted that the BH<sub>2</sub> rocking and wagging motions are heavily mixed with ring vibrations.

A number of bands were observed in the C-H stretching region and with the help of LDF calculations can be directly assigned. Many additional bands were observed in the CH<sub>2</sub> bending, twisting, and rocking regions, as well as in the region associated with ring skeletal deformations. As expected, none of these bands had a resolvable <sup>10</sup>B counterpart. Specific assignment of these bands is impossible without detailed isotopic labeling information. Even then, the modes are sufficiently mixed that clear assignments would be very difficult. Consequently, these modes are simply labeled CH<sub>2</sub> or "ring" in Table II. The lack of specific assignment of these bands does not detract from the identification of H<sub>2</sub>B=NC<sub>4</sub>H<sub>8</sub>, nor from the specific assignments which can be made for the H<sub>2</sub>B=N fragment of the molecule.

 $H_3B \cdot N(H)C_4H_8$ . Pyrrolidinoborane is an 18-atom molecule with 48 vibrational degrees of freedom and nearly  $C_s$  symmetry. Here, too, a complete set of assignments is not possible without much more extensive isotopic labeling. However, vibrations of the BH<sub>3</sub> subunit may be readily identified as well as certain other characteristic modes. The B-H stretching region of complexed BH<sub>3</sub> is between 2200 and 2400 cm<sup>-1</sup>, where several broad bands were observed. (Table III shows that the analogous modes of  $H_3B$ ·NC<sub>5</sub> $H_5$  also lie in this region.) LDF calculations also calculate B-H stretching modes in this region. Consequently, assignment is made. A specific characteristic mode of this adduct should be the N-H stretching mode which is expected above 3300 cm<sup>-1</sup>. One band was observed in this region, without <sup>10</sup>B counterpart, at 3342 cm<sup>-1</sup>. LDF calculations place this mode at 3312 cm<sup>-1</sup>, in good agreement. Hence, the 3342-cm<sup>-1</sup> band is assigned to the N-H stretching mode of the adduct.

Several additional bands fell in characteristic BH<sub>3</sub> bending regions and showed <sup>10</sup>B counterparts. Their assignments are listed in Table I. Additional modes characteristic of the CH<sub>2</sub> groups and the ring were detected. Some may be clearly assigned (e.g.,

the C-H stretching modes) while others can only be associated with the ring fragment of the complex. This is indicated in Table I.

One remaining motion of interest is the B-N stretching mode. This motion has been identified near 700 cm<sup>-1</sup> for complexes of BH<sub>3</sub> with several methylamines,<sup>7</sup> while for  $H_3B$ ·NC<sub>5</sub>H<sub>5</sub> it was assigned<sup>20</sup> at 1082 cm<sup>-1</sup>. This absorption is generally weak, due to the nature of the dative bond in the complex. A weaker, broad absorption was observed at 1097 cm<sup>-1</sup> in the present study and is a candidate for this mode. LDF calculations place the B-N stretch at 1080 cm<sup>-1</sup>, quite close to the observed band. Thus, assignment to the B-N stretch is quite reasonable. However, it is unclear why the analogous mode for the  $H_3B$ ·N(CH<sub>3</sub>)<sub>3</sub> complex was observed 400 cm<sup>-1</sup> to lower energy. It is possible that the present complex is significantly more strongly bound, but there is not direct evidence to that effect. Also, additional modes of the  $H_3B \cdot NC_4H_8$  complex are expected in this region. Thus, assignments of the 1097-cm<sup>-1</sup> band to the B-N stretch must be viewed as tentative at this time.

Mechanistic Considerations. Previous studies<sup>6-10,26</sup> of the pyrolytic reaction of  $B_2H_6$  with electron donors (bases) led to a proposed mechanism in which an initial BH<sub>3</sub> complex with the base was formed. This was followed by  $H_2$  or  $CH_4$  elimination (depending on the base), forming the intermediate borane compound. In some cases, further reaction occurred at very high pyrolysis temperatures. For a few systems, the initial complex was observed, while for most of the others, only the elimination product was seen. The present study of the  $B_2H_6/C_4H_9N$  system provides clear support for this mechanism: the complex alone was seen at low pyrolysis temperatures (ambient to 40 °C) while at intermediate temperatures both the complex and the H<sub>2</sub> elimination product were seen. At high pyrolysis temperatures, only the latter species was observed. It should be noted that Burg and Good reportedly synthesized  $H_2B=NC_4H_8$  by heating the  $H_3B$ ·NC<sub>4</sub> $H_9$  adduct to 135 °C for several hours to permit reaction and H<sub>2</sub> elimination.

It is interesting to compare the reactivities of the three cyclic amines in the present study. Pyrrolidine formed first an adduct with  $BH_3$  followed by  $H_2$  elimination. Pyridine formed the  $BH_3$ adduct which did not undergo further reaction. On the other hand, pyrrole did not form the BH<sub>3</sub> adduct and consequently could not undergo further reaction. The result that the  $H_3B \cdot NC_5H_5$  complex did not react further is reasonable in that there are no hydrogens on the nitrogen to participate in  $H_2$ elimination. It is the result for the  $B_2H_6/C_4H_5N$  that is perhaps surprising. This compound is apparently quite similar to pyridine and pyrrolidine, is relatively basic, and contains a hydrogen bound to the nitrogen. Also, in solution the room temperature reaction of  $B_2H_6$  with pyrrole is known<sup>27</sup> to form  $H_2BNC_4H_4$ , a compound

that is also commercially available. Nonetheless, no reaction to form the complex or further product was observed. The explanation for this unexpected behavior may lie with the fact that while there is a lone pair of electrons on the nitrogen in each of the cyclic amines studied, only in pyrrole does this lone pair participate in the aromaticity of the ring.<sup>28</sup> Thus, complex formation to BH<sub>3</sub> would require disruption of the aromatic character of the pyrrole ring. Thus, complex formation in the gas phase (absence of solvation) may be energetically unfavorable or have a high barrier to formation (and hence occur slowly). While not conclusive, this provides a reasonable rationale for the very different observed reactivity of pyrrole in the present study.

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