

Infrared Spectra and Structure of Beryllium Borohydride

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Abstract: Infrared spectral assignments for beryllium borohydride vapor are made by analogy with compounds of known structure and with the aid of deuterium and ^{10}B substitution. The structure of beryllium borohydride consists of an approximate equilateral triangular arrangement of metal atoms. Each boron is bound to beryllium *via* a double hydrogen bridge and all four bridging hydrogens are in a plane perpendicular to the plane of the three metal atoms. Each boron has two terminal hydrogens and all four terminal hydrogens lie in the plane of the metal atoms. The molecule has C_{2v} symmetry. A gas-phase infrared study of the trimethylamine adduct of beryllium borohydride supports these conclusions and shows the nonexistence of beryllium-hydrogen terminal bonds in beryllium borohydride.

Beryllium borohydride was first prepared in 1940 by Burg and Schlesinger.¹ Their synthesis was based on the analogous reaction of trimethylaluminum with diborane to form aluminum borohydride. Beryllium borohydride was found to be similar to aluminum borohydride in that it inflames violently in air and reacts vigorously with water. Beryllium borohydride was observed to be less volatile and to have a melting point at least 180° higher than that of aluminum borohydride. Because of the different physical properties, they reasoned that beryllium borohydride may be more highly polar in character than aluminum borohydride.

In 1946 an electron diffraction study resulted in a structure consistent with the observed five maxima and four minima.² The model presented was a linear H-B-Be-B-H skeleton with the remaining six hydrogens around the beryllium on the corners of a distorted octahedron.

Some infrared absorption bands of beryllium borohydride were published in 1949. Two of these bands (*e.g.*, 1500 and 2000 cm^{-1}) were considered evidence for a bridged structure.³

Also in 1949 an infrared study showed the structure of aluminum borohydride to consist of three equivalent borohydride groups, each of which is bound to the aluminum *via* double a hydrogen bridge.⁴ On the basis of a linear boron-beryllium-boron skeleton, it was proposed that beryllium borohydride has a structure in which the linear metal skeleton is joined *via* double hydrogen bridges, with each boron having two terminal hydrogens.⁵ This arrangement required approximate tetrahedral metal atoms, and because of its similarity to the known diborane structure, it was termed the "classic structure" (Figure 1, structure I). Interestingly, this structure too was found to fit the electron diffraction curve.⁶

An X-ray diffraction study subsequently showed that the unit cell contains 16 molecules in general positions, and a structure could not be determined.⁷

In 1968 a new electron diffraction determination showed the metal atoms to be located on the corners

of an approximate equilateral triangle.⁸ In this structure a "beryllium hydride" molecule seemed to combine with a diborane molecule causing the beryllium atom to be bonded—at least to some extent—to six hydrogen atoms and two boron atoms. Energy calculations for this structure indicated weak bonding interactions between the "BeH₂" and "diborane" moieties.^{9,10} This structure (Figure 1, structure II) was criticized because of the unusually long beryllium-hydrogen "bonds" required for electron diffraction curve fitting. An alternate structure was considered in which the metal atoms formed an approximate equilateral triangle connected *via* single hydrogen bridges and having a plane of symmetry.¹¹ This structure was a specific conformer of an earlier structure proposed by Coates¹² which was later called into question owing to chemical evidence.¹³

Infrared evidence (indicating BH₂ terminal groups) and mass spectral data led us to propose structure III, Figure 1, in 1969.¹⁴ This structure still retained the triangular arrangement of metal atoms and was found to satisfactorily fit the original electron diffraction data of Haaland.⁸

Later in 1969 a gas-phase infrared study, matrix infrared study, and dipole moment study agreed with a C_{2v} symmetry assignment.¹⁵ Apparently unaware of structure III, the authors evaluated their data as consistent with structure II rather than structure I (the classical structure). Subsequently, an electron deflection experiment verified the presence of a dipole moment.¹⁶

A recent electron diffraction study¹⁷ failed to reproduce the results reported in 1968, but rather gave evidence for a long metal-metal distance (at about 3.6 Å) which *may* imply a linear molecule. Similar results have been obtained in other studies.¹⁸ Attempts to

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(3) W. C. Price, *J. Chem. Phys.*, **17**, 217 (1949).

(4) W. C. Price, *ibid.*, **17**, 1044 (1949).

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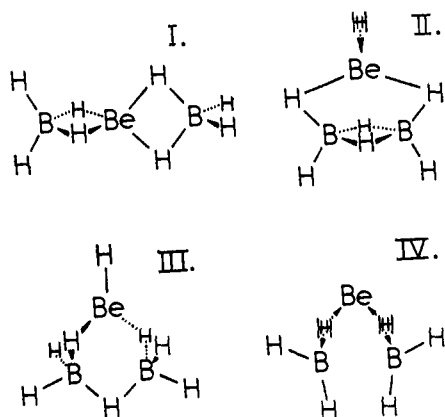


Figure 1. Various suggested structures for beryllium borohydride.

record the microwave spectrum yielded no spectrum at all,¹⁹ although serious decomposition problems likely affected the experiment.

In view of these recent experiments one may be tempted to abandon the equilateral triangle of metal atoms in the structure of beryllium borohydride. The infrared spectral data presented in this paper can only be consistent with such a triangular metal arrangement, however.

Experimental Section

Commercial beryllium chloride was found to be very impure. About 80% of the material obtained from common sources would not sublime at 300°. Thus beryllium chloride was synthesized. Beryllium metal (9 g) was placed in the reaction chamber and heated with gas burners, while a mixture of one part chlorine and three parts nitrogen gas flowed through the tube. The resulting beryllium chloride sublimed into the collection chamber with the help of selected heating in areas of beryllium chloride accumulation. A yield of 90% (72 g) was obtained. The resulting beryllium chloride exhibited excellent solubility properties in ether and was almost entirely sublimable at 300°.

Be(BH₄)₂. Beryllium borohydride was prepared by two distinctly different methods. For the preparation of ¹¹B beryllium borohydride (and borodeuteride) the method of heating lithium borohydride (and borodeuteride) with beryllium chloride (solid state reaction) was used.²⁰ In a representative reaction, 0.2 g of lithium borohydride and 1 g of beryllium chloride were heated slowly from 90 to 140°. No yield data were recorded. For the preparation of ¹⁰B beryllium borohydride (and borodeuteride) the diborane reaction with dimethylberyllium was used.¹ The preparation of dimethylberyllium has already been described,¹ as well as the synthesis of ¹⁰B diborane, and that of ¹⁰B methylberyllium borohydride.²¹ This volatile compound was transferred into a 56-ml reaction bulb (equipped with a vacuum stopcock) and 3 atm of ¹⁰B diborane added. The entire apparatus was heated to 50° for 12 hr and only ¹⁰B trimethylboron, ¹⁰B diborane, and pure ¹⁰B beryllium borohydride were observed. The mixture was pumped on at -80°, leaving only the ¹⁰B beryllium borohydride behind. These forcing conditions were probably not necessary, as discovered later, but for consistent results and complete conversion these conditions were used.

The trimethylamine 1:1 adduct of beryllium borohydride was conveniently prepared in the infrared gas cell by cooling the small tube, which connects the stopcock to the cell, with Dry Ice and condensing in a volume-measured amount of beryllium borohydride. The amount condensed in was just double the amount necessary to saturate the cell at room temperature. Trimethylamine was then allowed into the cell at a pressure of 20 mm, and the mixture was allowed to warm to room temperature. By warming the resulting solid, a liquid was seen to form which was the desired product, the

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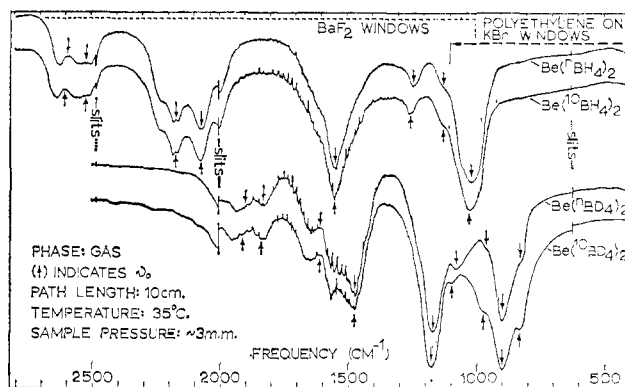


Figure 2. Infrared spectra of beryllium borohydride.

trimethylamine 1:1 adduct of beryllium borohydride. Excess trimethylamine and unreacted beryllium borohydride were pumped off while the small tube was maintained at 0° (ordinary ice). The high vapor pressures of trimethylamine and beryllium borohydride made their removal very easy.

Sources of reagents have been previously cited.²¹ Since beryllium borohydride is very reactive, even with potassium bromide and silicone materials, a special infrared cell construction was employed.²¹

Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. All operations were carried out on a vacuum line or in an inert atmosphere enclosure, owing to the pyrophoric nature of these compounds.

Results and Discussion

Infrared Spectra of Unsaturated Vapors. The unsaturated gas-phase infrared spectra of the four isotopically different beryllium borohydride compounds are shown in Figure 2. A comparison of the individual bands with the corresponding aluminum borohydride bands is tabulated in Table I, and the deuterium and

Table I. Infrared Assignments of Beryllium Borohydride by Analogy

Be(¹¹ BH ₄) ₂ , cm ⁻¹	Al(¹¹ BH ₄) ₃ , ^a cm ⁻¹	Assignment
2598 (m)	2559 (s)	B-H asym str
2521 (m)	2493 (s)	B-H sym str
2172 (s)	2154 ^b (s)	MH ₂ B br exp
2069 (s)	2031 ^b (s)	MH ₂ B asym br str
1995 (m)		Complex br mode (?)
1545 (vs)	1500 (vs)	MH ₂ B sym br str
1245 (m)	1255 (w)	(BH ₂ rock)
1125 (m)	1114 (vs)	BH ₂ def
1014 (w)	603 (w)	M-B asym str
1014 (vs)	978 (m)	BH ₂ rock

^a Values from ref 4. ^b This assignment is the reverse of that of ref 4.

boron-10 shifts of the individual bands are presented in Table II. By comparing the spectra with the tables, one notes that the band center (ν_0) does not necessarily occur at a maximum in the absorption curve (e.g., the 2598- and 2172-cm⁻¹ bands). The relatively low resolution spectra of beryllium borohydride (Figure 2) could be interpreted in two significantly different ways. The first interpretation is that each absorption maximum represents a vibrational band center (ν_0) with nonresolved rotational envelopes contained within the maximum. This relatively narrow unresolved band would be a result of the closely spaced rotational energy

Table II. Infrared Assignments of Beryllium Borohydride Using Deuterium and Boron-10 Shifts

Contour type	Be(n BH $_4$) $_2$, cm $^{-1}$	Be(10 BH $_4$) $_2$, cm $^{-1}$	Be(n BD $_4$) $_2$, cm $^{-1}$	Be(10 BD $_4$) $_2$, cm $^{-1}$	Deuterium shift (H/D), cm $^{-1}$	10 B shift, cm $^{-1}$	Assignments
B	2598 (m)	2606 (m)	1894 (m)	1904 (m)	1.37	+8 + 10	B-H asym str
A	2521 (m)	2526 (m)	1822 (m)	1835 (m)	1.38	+5 + 13	B-H sym str
B	2172 (s)	2174 (s)	1605 (s)	1607 (s)	1.35	+2 + 2	BeH $_2$ B bridge exp
C	2069 (s)	2074 (s)	1466 (s)	1471 (s)	1.41	+5 + 5	BeH $_2$ B asym br str
	1995 (m)	1999 (m)				+4	Complex br mode (?)
C	1545 (vs)	1547 (vs)	1164 (vs)	1165 (vs)	1.33	+2 + 1	BeH $_2$ B sym br str
	1245 (m)	1260 (m)	1073 (m)	1091 (m)	1.16	+15 + 18	BH $_2$ rock
	1125 (m)	1125 (m)	830 (m)	830 (m)	1.36	0 0	BH $_2$ def
	1014 (w)	1018 (w)	962 (w)	970 (w)	1.05	+4 + 8	Be-B asym str
	1014 (vs)	1018 (vs)	892 (vs)	892 (vs)	1.14	+4 0	BH $_2$ rock

changes present in a structure with at least one large moment of inertia. This interpretation has been applied to the gas-phase infrared spectrum of beryllium borohydride.

The second interpretation is that certain of the maxima represent PQR or PR rotational contours and that the band center (ν_0) is located at a maximum or minimum depending if the band is type A and C or B, respectively. A large rotational energy separation (and consequently large PR maxima separation) is consistent with a structure with only small moments of inertia (where $E' - E'' = \hbar^2/I[J'(J' + 1) - J''(J'' + 1)]$).²² By using moderate resolution (normal slit width reduced to one-half the survey mode) and low sample pressure (1 ± 0.2 mm), the rotational contours of the terminal BH $_2$ stretches (asymmetric-PR and symmetric-PQR) were resolved (Figure 3). Resolution of rotational envelopes permits the determination of band centers (ν_0) and the determination of the number of bands. Three criteria used for the assignments are: (a) location of vibrational band centers (ν_0) by comparison of observed rotational contours with those in diborane; (b) comparison of band positions with band positions in aluminum borohydride, which has been shown by infrared⁴ and Raman²³ spectroscopy to contain AlH $_2$ B bridging groups and BH $_2$ terminal groups; and (c) correlation of deuterium and boron-10 isotopic shifts. By applying these criteria, the structure of beryllium borohydride is shown to contain BH $_2$ terminal groups and BeH $_2$ B bridging groups.^{23a}

The BH $_2$ terminal stretching frequencies of beryllium borohydride at 2598 (asymmetric B-H stretch) and 2521 cm $^{-1}$ (symmetric B-H stretch) have, respectively, type B and type A rotational contours as do the analogous bands at 2625 (type B) and 2558 cm $^{-1}$ (type A) in diborane.²⁴ The BH $_2$ terminal stretching modes of aluminum borohydride occur at 2559 and 2493 cm $^{-1}$ and further establish the assignment.

The deuterium shift ratio of 1.37 and boron-10 shift range of +5 to +13 cm $^{-1}$ of the 2598 and 2521-cm $^{-1}$ bands are consistent with the expected large hydrogen movement and moderate boron movement during these BH $_2$ terminal stretches (the two hydrogens of the

BH $_2$ terminal group comprising about $1/6$ th the mass of the entire group.)

In beryllium borohydride the BH $_2$ terminal deformation at 1125 cm $^{-1}$ and the rocking modes at 1245 and 1014 cm $^{-1}$ correspond to the 1114- (BH $_2$ deformation),

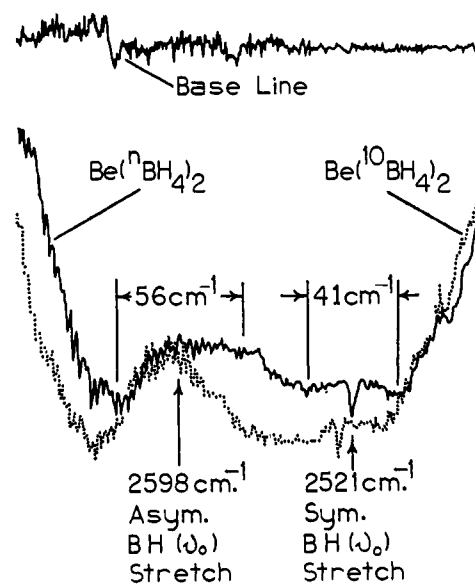


Figure 3. Rotational envelopes of the terminal B-H stretching modes in the infrared spectra of beryllium borohydride.

1255- (unassigned), and 978-cm $^{-1}$ (BH $_2$ rocking mode) bands of aluminum borohydride.⁴ Absence of a band in the 890-910-cm $^{-1}$ region (characteristic of B-H single terminal groups) further indicates the absence of BH terminal groups in beryllium borohydride.²⁵ Deuterium and boron-10 shifts of these bands clearly differentiate which are deformation and which are rocking modes. The 1125-cm $^{-1}$ band shows a deuterium shift ratio of 1.36 and a boron-10 shift of zero. These are the expected shifts of a BH $_2$ deformation mode, which consists primarily of hydrogen movement. The 1245-cm $^{-1}$ band shows a deuterium shift ratio of 1.15-1.16 and a boron-10 shift of +15 to +18 cm $^{-1}$, which are the characteristic shifts of a BH $_2$ rocking mode, which involves considerable boron movement. The low isotopic shifts (deuterium shift ratio of 1.14 and boron-10 shift of zero) of the 1014-cm $^{-1}$ band appear

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(23) A. R. Emery and R. C. Taylor, *Spectrochim. Acta*, **16**, 1455 (1960).

(23a) NOTE ADDED IN PROOF. Dr. J. W. Nibler has pointed out that a small contamination of diborane is likely present in these spectra. Our basic conclusions should not be altered, however.

(24) W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948).

to reflect a small boron movement *and* a small hydrogen movement during the vibration. Because boron motion is likely to be influenced by bridging vibrations, the low boron-10 shift may not demonstrate small boron movement. The above infrared assignments of one BH_2 deformation mode (1125 cm^{-1}) and two BH_2 rocking modes (1245 and 1014 cm^{-1}) are consistent with the prediction of one BH_2 deformation mode (ν_{19}) and two BH_2 rocking modes (ν_{20} and ν_{13}) for aluminum borohydride.²³

The assignment of the BeH_2B bridging modes in the region $2300\text{--}1500\text{ cm}^{-1}$ is made with reference to the very similar bands of aluminum borohydride.⁴ These assignments were considered in detail in the study of methylberyllium borohydride.²¹

Because beryllium borohydride exhibits similar rotational contours to those of diborane in the terminal BH_2 stretching modes and because the terminal and bridging hydrogens in beryllium borohydride likely lie in mutually, nearly perpendicular planes, similar rotational contours may be expected in the asymmetric bridge and bridge expansion modes (the bridges being BeH_2B and BH_2B). The asymmetric bridge stretch in diborane exhibits a C-type contour (strong central Q branch), whereas the bridge expansion mode exhibits a B-type contour (P and R branches with a Q-branch intensity of zero).²⁴ Thus in the $1900\text{--}2300\text{ cm}^{-1}$ region of beryllium borohydride the most intense absorption maximum at 2069 cm^{-1} (C-type contour) is assigned to the asymmetric BeH_2B bridge stretch. The corresponding most intense absorption maximum in the deuterated spectrum is observed at 1466 cm^{-1} .

The minimum at 2172 cm^{-1} (B-type contour) is assigned to the BeH_2B bridge expansion mode. This particular minimum is chosen because *each* P and R branch exhibits *two* maxima in the hydrogen compounds and *each* P and R branch exhibits *one* maximum in the deuterated compounds.^{26,27} The band center in the deuterated spectrum is located at the 1605 cm^{-1} minimum. The deuterium shift ratio range of 1.33 to 1.41 and boron-10 shift range of $+1$ to $+5\text{ cm}^{-1}$ of the 1545 cm^{-1} , 2069 cm^{-1} , and 2172 cm^{-1} bands are consistent with the expected large hydrogen movement and small boron movement during the BeH_2B bridge vibrations. The large hydrogen movement and small boron movement are probably the result of relative mass effects. The two hydrogens of the BeH_2B group comprise only about $1/10$ th the mass of the entire group. The great intensity of these bands is attributed to the large local dipoles, which result from the displacement of the electron-deficient bridges.⁴

The only unassigned absorption maximum in the $1900\text{--}2300\text{ cm}^{-1}$ region of infrared spectrum of beryllium borohydride is the 1995 cm^{-1} absorption. From the beryllium borohydride and beryllium borodeuteride spectra one might suppose that the corresponding maximum in the deuterated spectrum falls under the 1466 cm^{-1} peak and has a deuterated shift ratio of about 1.36. This band may be a complex bridging mode. The observed boron-10 shift of $+4\text{ cm}^{-1}$ of this band indicates that this band does *not* arise from a *Be-H terminal group* (*vide infra*), which should show no boron-10 shift.

(26) R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, **6**, 711 (1938).

(27) T. Ueda and T. Shimanouchi, *J. Mol. Spectrosc.*, **28**, 350 (1968).

The remaining absorption in the spectrum of beryllium borohydride is a *weak* band at about 1014 cm^{-1} , which is obscured by the much stronger BH_2 rocking mode centered at 1014 cm^{-1} . Two experimental observations indicate the presence of this weak band. First, the strong BH_2 rocking mode centered at 1014 cm^{-1} is much broader than its corresponding strong band at 892 cm^{-1} in beryllium borodeuteride. Second, the beryllium borodeuteride spectrum has a band at 962 cm^{-1} , which *apparently* has no analog in the beryllium borohydride spectrum.

The weak 1014 cm^{-1} band of beryllium borohydride is assigned to the Be-B asymmetric stretch (analogous to the 600 cm^{-1} Al-B asymmetric stretch in aluminum borohydride). The deuterium shift ratio of 1.05 and boron-10 shift (deuterated compounds) of $+8\text{ cm}^{-1}$ support the assignment of Be-B asymmetric stretch for the 1014 cm^{-1} band. A reduced mass calculation in which the beryllium is one mass and the borohydride group, *as a unit*, is the second mass leads to the prediction of a deuterium shift ratio of 1.04 and a boron-10 shift of $+9\text{ cm}^{-1}$.

It is thus seen that the band assignments are consistent for structures I and IV (Figure 1), and the question of the choice between them arises. We shall attempt to resolve this question by calculating the expected P-R maxima separations for the B-H symmetric stretching frequency (using models of structure I and IV) and comparing these with the experimental P-R maximum separation of $41 \pm 3\text{ cm}^{-1}$ for the 2521 cm^{-1} band (Figure 3).

For structure I, the following parameters are used:¹⁴ Be-B, 1.8 \AA , Be-H', 1.4 \AA , B-H', 1.3 \AA , B-H, 1.2 \AA ; and $\angle\text{H-B-H}$ (terminal), 120° . The moments of inertia may thus be calculated: $I_A = 14.1 \times 10^{-40}$, $I_B = I_C = 170 \times 10^{-40}\text{ g cm}^2$. Using the method of Gerhard and Dennison²² an *S* parameter of 1.08 is calculated, and from $\Delta\nu = S[kT/I_C]^{1/2}/\pi$ a value of $\Delta\nu$ of 18.1 cm^{-1} (19.2 cm^{-1} for the ^{10}B compound) is calculated. This clearly is *not* consistent with the experimentally observed P-R maxima separation of $41 \pm 3\text{ cm}^{-1}$ (Figure 3).

Using the above bond lengths and angles for structure IV (Figure 1), but with a $\angle\text{B-Be-B}$ of 57° , the calculated moments of inertia are: $I_A = 43.7 \times 10^{-40}$, $I_B = 50.4 \times 10^{-40}$, and $I_C = 83.1 \times 10^{-40}\text{ g cm}^2$. Because the B-H symmetric stretch for structure II is a perpendicular band (rather than a parallel band as in structure I), the Gerhard-Dennison method cannot be used to calculate the P-R maxima separation. The Badger-Zumwalt method,²⁶ however, can be used to calculate the P-R maxima separation of the B-H symmetric stretch, which has A-type contours. Parameters ρ (0.548) and *S* (0.449) (a different *S* from that used in the Gerhard-Dennison method) are calculated by this method and an *x* value of 0.81 is obtained from graphs.²⁶ This *x* is equal to $(\nu - \nu_0)\pi[2I_B/kT]^{1/2}$, where $\Delta\nu = 2(\nu - \nu_0)$. A value of $\Delta\nu$ of 35.4 cm^{-1} (36.2 cm^{-1} for the ^{10}B compound) is thus obtained for structure IV. This calculated P-R maxima separation of 35.4 cm^{-1} qualitatively agrees with the experimental P-R maxima separation of $41 \pm 3\text{ cm}^{-1}$. Structure IV is thus consistent with these data whereas structure I is not.

This structure contains an approximately equilateral

arrangement of metal atoms, as earlier suggested.⁸ Because of the limited space, each pair of hydrogens in the BeH_2B bridge must lie on a line which is perpendicular to the plane which contains the three metal atoms. Because the infrared asymmetric and symmetric B-H stretches of beryllium borohydride show the same type rotational contours as diborane, the hydrogens of the BH_2 terminal groups likely have an orientation which is very similar to that of diborane. The symmetric B-H stretch of the BH_2 terminal group of structure IV results in a dipole moment change, which is primarily parallel to the *A* axis, resulting in the observed type A rotational contour. The shape of the type A rotational contours published by Badger and Zumwalt²⁶ for ρ and *S* parameters of approximately 0.5 (our calculated values from the model) indeed have a very similar appearance to the experimental rotational contours. The asymmetric B-H stretch of the BH_2 terminal groups of structure IV results in a dipole moment change which is parallel to the *B* axis, resulting in the observed type B rotational contour. All of the infrared data taken in this work are thus shown to be consistent with the proposed structure IV.

Other experimental measurements on beryllium borohydride are consistent with structure IV. The melting point of beryllium borohydride, being at least 180° higher than that of aluminum borohydride, is consistent with structure IV, which likely has a large dipole moment.¹ Using a dielectric cell, a $2.1 \pm 0.5\text{-D}$ dipole moment was obtained for beryllium borohydride.¹⁶

The B-B distance of 1.7 \AA in structure IV, being very similar to the B-B "single bond" distance of $1.73\text{--}1.76 \text{ \AA}$ (electron diffraction) in $\text{Cl}_2\text{B-BCl}_2$, indicates considerable boron-boron interaction.²⁸ A boron-boron interaction seems to be a plausible explanation for such a small experimentally determined boron-beryllium-boron angle. By counting bonding electrons, 2 in each of the 4 terminal B-H bonds, and 2 in each of the 4 three-center bridge bonds, one soon accounts for all 16 bonding electrons in beryllium borohydride. Clearly, according to present views, there are no electrons available which could form a boron-boron bond. Some interesting calculations on diborane, in which the boron-boron distance is 1.79 \AA , indicate considerable boron-boron interaction.^{29,30}

Alternatively, one might account for the unexpected bent structure with a dynamic vibrational argument. This would call for the borohydride groups vibrating rapidly through an "equilibrium" linear structure to spend most of their time in the extrema of the vibration which would represent two potential energy minima.

Infrared Spectra of Saturated Vapors. When saturated vapors of beryllium borohydride are examined, dramatic changes were noted in the infrared spectra, only in the B-H stretching and bridge expansion regions (Figure 4). As the sample pressure is increased, the rotational contours become obscured by broadening. Further sample pressure increase, to the point of saturation, causes new, sharp bands to emerge, such as at 2579 and 2503 cm^{-1} in the spectrum of $\text{Be}^{(10)}\text{BH}_4)_2$. These sharp bands are consistent with molecular struc-

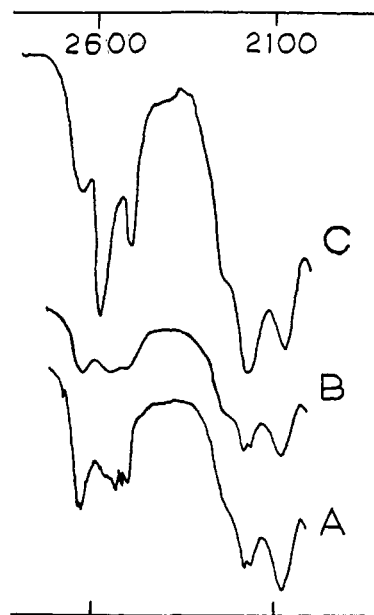


Figure 4. Infrared spectra of $\text{Be}^{(10)}\text{BH}_4)_2$ vapors at 35° at various pressures: (A) 0.6 mm , $20\times$ expansion; (B) 3 mm , $2.5\times$ expansion; (C) saturated vapors, $1\times$ expansion.

tures with relatively high moments of inertia, for example, dimer, trimer, etc. The possibilities of di- or trimerization should not be unexpected for species of the type proposed (structure IV). This may account for the recent electron diffraction data^{17,18} which show a long 3.6-\AA distance. Studies of the saturated vapors were not continued owing to their inherent complexity.

Spectrum of the Trimethylamine Adduct. A comparison of the band assignments for gas-phase beryllium borohydride and its 1:1 trimethylamine adduct (saturated vapors) is summarized in Table III (BaF_2 region

Table III. Comparison of Infrared Boron-Hydrogen Absorptions of Beryllium Borohydride and Its 1:1 Trimethylamine Adduct

$\text{Be}^{(10)}\text{BH}_4)_2$, cm^{-1}	$(\text{CH}_3)_3\text{N-Be}^{(10)}\text{BH}_4)_2$, cm^{-1}	Assignment
2598 (m)	2505 (vs)	B-H asym str
2521 (m)	2439 (s)	B-H sym str
2172 (s)	2162 (sh)	BeH_2B br exp
2069 (s)	2133 (vs)	BeH_2B asym br str
1995 (m)	2032 (m)	Complex br mode (?)
1545 (vs)	1468 (vs)	BeH_2B sym br str
1245 (m)	1291 (m)	BH_2 rock
1125 (m)	1141 (s)	BH_2 def

only). A comparison of the individual bands of the adduct with the borohydride shows that the terminal BH_2 and bridge BeH_2B groups remain intact in the adduct. In the adduct the BH_2 terminal groups are shown by the asymmetric B-H stretch (2505 cm^{-1}), the symmetric B-H stretch (2439 cm^{-1}), the BH_2 rocking mode (1291 cm^{-1}), and the BH_2 deformation mode (1141 cm^{-1}). It is also clear that the BeH_2B bridge is intact, as evidenced by the asymmetric (2133 cm^{-1}) and symmetric (1468 cm^{-1}) BeH_2B bridge stretching modes and the BeH_2B bridge expansion mode (2162

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cm^{-1}).⁴ For these and other reasons, we assume a Be-N bond with the beryllium atom in a roughly trigonal environment (two borohydride groups and one trimethylamine).

The net result of forming the trimethylamine 1:1 adduct of beryllium borohydride is to produce an increased ionic character in the borohydride group. This is indicated (*vide supra*) by observed shifts of the two terminal B-H stretches and BeH_2B asymmetric bridge stretch, which shift toward the single B-H stretching frequency of the borohydride ion at 2270–2320 cm^{-1} .⁴ Similarly, the BH deformation modes and the BeH_2B symmetric bridge stretch shift toward the single B-H deformation frequency of the free borohydride ion at 1080–1096 cm^{-1} .⁴

Comparison of the spectra of beryllium borohydride and the 1:1 trimethylamine adduct indicates the absence of terminal Be-H groups in these compounds. Be-

cause two independent studies have established that the terminal Be-H stretching mode occurs in the 1740–1807- cm^{-1} region, one reasonably expects a Be-H terminal group to have an absorption in the 1600–2000- cm^{-1} region.^{31,32} Since the nitrogen is bound to the beryllium, one would expect a significant decrease in the Be-H terminal stretching frequency if such a terminal group were present. No such Be-H terminal group is indicated by these data.

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Reaction of Xenon Difluoride with Aromatic Compounds. II. The Use of Xenon Difluoride as a Selective Fluorinating Agent^{1a}

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Abstract: Xenon difluoride is shown to react with a variety of substituted benzenes in CCl_4 or CH_2Cl_2 to produce fluorobenzenes in good yield. The reaction is catalyzed by HF and does not proceed without it. Substituent effects are similar to those observed in electrophilic aromatic substitution reactions. The use of xenon difluoride often offers an attractive alternative route to the conventional Balz-Schiemann reaction for the preparation of fluorinated aromatic compounds.

One of the most interesting problems in organic fluorine chemistry has been the lack of a general selective fluorinating agent for aromatic compounds. It has been stated that "Fluorine differs from other halogens in that it cannot be introduced into an aromatic ring by direct reaction because of its great reactivity. This has necessitated the development of special methods and has been both difficult and slow."² In a few isolated experiments, ring fluorination of suitably activated compounds has been achieved without loss of aromaticity. For example, reaction of 2,4-dinitroaniline with fluorine in HF gave small yields of 1-difluoroamino-5-fluoro-2,4-dinitrobenzene.³ Fluoroxytrifluoromethane (CF_3OF) reacts with salicylic acid to give a 4:1 mixture of 3- and 5-fluorosalicic acid in 70% yield.⁴ Most reactive fluorinating agents

such as fluorine,⁵ high-valency metal fluorides,⁶ and halogen fluorides⁷ yield mostly fluorine addition products and tars, although it has been reported that ClF_3 in the presence of CoF_2 reacts with substituted benzenes to give about a 20% yield of fluoro substitution products.⁷

Recently, however, Grakauskas has shown that fluorine, in solution and well below room temperature, can be used to effect electrophilic substitution reaction.⁸ The difficulty with known fluorinating agents in effecting electrophilic aromatic substitution is certainly related to the difficulty in forming F^+ (ionization potential of $\text{F} = 401.5$ eV; ionization potential of $\text{Cl} = 300$ eV).⁹ An alternative explanation for the lack of selectivity in the reactions of strong fluorinating agents may involve the thermodynamics of the reac-

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