

# Infrared Absorption Spectrum of Trimethylborane

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The infrared absorption spectrum of gaseous trimethylborane,  $B(CH_3)_3$ , has been observed in the 2- to 40-micron spectral region. Vibrational assignments have been made for infrared bands, as well as for the Raman lines reported by other investigators. The perfect gas entropy was calculated for a temperature of  $199.92^\circ K$  and compared with the experimental value. Barriers to internal rotation of methyl groups of about 750 or 1,640 calories per mole are calculated for structures with or without a threefold axis of symmetry.

## 1. Introduction

This study of the infrared spectrum of gaseous trimethylborane was undertaken as part of a program of the National Bureau of Standards for the investigation of chemical and physical properties of boron compounds.

The infrared and Raman spectra of trimethylborane were first reported by Goubeau and Becher [1].<sup>1</sup> Their data were used by Siebert [2] in a normal coordinate treatment. The infrared spectrum of Goubeau and Becher does not extend beyond about  $600\text{ cm}^{-1}$ , and it contains impurity bands not observed in the present study. Accordingly, it seemed desirable to repeat and extend the measurements. Very recently Levy [3] measured the very near infrared spectrum of trimethylborane and other boron compounds.

## 2. Experimental Procedure

The samples of trimethylborane were prepared by A. R. Glasgow, Jr., and G. S. Ross, Sr., of the Bureau's Pure Substances Section by reaction of hydrogen chloride with the ammonia adduct  $B(CH_3)_3 \cdot NH_3$ . After subsequent purification [4], purities of two lots were determined calorimetrically by G. T. Furukawa of the Thermodynamics Section and found to be  $99.7 \pm 0.1$  and  $99.9 \pm 0.1$  percent. These lots were indistinguishable spectroscopically.

The material was stored as liquid at reduced temperature in stainless-steel cylinders and was distilled into an auxiliary glass bulb immediately before admission into the absorption cell. Purification procedures were monitored by obtaining spectra after successive operations on samples from both the liquid and gas phases in the cylinder. This procedure was of value in the identification of impurity bands. Pressures were measured with a mercury manometer.

Spectra were obtained with a Perkin-Elmer model 21 double-beam spectrophotometer equipped with

prisms of sodium chloride and cesium bromide for the 2- to  $15\text{-}\mu$  and  $15\text{-}$  to  $40\text{-}\mu$  regions, respectively. Stray radiation encountered when using the cesium bromide prism was limited to 2 percent or less for wavelengths less than  $38\text{ }\mu$  by means of reststrahlen filters of lithium fluoride and calcium fluoride. A Perkin-Elmer model 12B spectrometer with a lithium fluoride prism was also used for the near infrared region. A potassium bromide prism was not required because no bands were observed between  $15$  and  $25\text{ }\mu$ . Standard Perkin-Elmer gas-cell bodies of nickel-plated brass were used. Potassium bromide and cesium bromide windows were mounted with silicone rubber gaskets coated with silicone grease, with polychlorotrifluoroethylene wax, or with a beeswax-rosin mixture.

## 3. Results

Trimethylborane is very reactive with oxygen and ignites spontaneously in air. Very slow decomposition of the sample in the cell was observed, probably due to slight air leakage at the window seals. No spectral evidence was found for the formation of methane, ethane, ethylene, or carbon dioxide during this reaction. The appearance of a band near  $1,370\text{ cm}^{-1}$  is very likely associated with the formation of  $B-O-C$  bonds [5], suggesting that boron methoxides are produced by slow oxidation. Additional bands appeared at  $1,479$ ,  $1,220$ ,  $1,062$ – $1,055$ – $1,048$  (PQR-like structure),  $950$ ,  $787$ , and  $590\text{ cm}^{-1}$ . When purified material was stored for several weeks at reduced temperature and reexamined, none of the above bands was seen except  $787\text{ cm}^{-1}$ . An additional band was found at  $730\text{ cm}^{-1}$ .

Goubeau and Becher reported medium to strong bands at  $620$ ,  $635$ ,  $648$ ,  $667$ ,  $720$ , and  $800\text{ cm}^{-1}$ , which were not observed in the present study even at higher pressures. Furthermore, several bands were not resolved in their spectrum because sufficiently low pressure was not used.

The sodium chloride and cesium bromide spectra are shown in figure 1, and the complete spectrum is tabulated in table 1, along with the Raman spectrum of Goubeau and Becher.

<sup>1</sup> Figures in brackets indicates the literature references at the end of this paper.

TABLE 1. *Vibrational frequencies and assignments for trimethylborane*

(w, weak; m, medium; s, strong; v, very; b, broad; sh, shoulder)

Raman (liquid)	Infrared (gas)	$C_s$ symmetry	Assignment	$C_{3h}$ symmetry
$cm^{-1}$ 320 4b	$cm^{-1}$ 320 m 336 m 345 sh	$\nu_{17}(a')$ , $\nu_{31}(a'')$ $\nu_{16}(a')$ $\nu_{31}(a'')$ ?, $\nu_{16}(a')$ B <sup>10</sup>	$C_3B$ bending $C_3B$ out-of-plane $C_3B^{10}$ out-of-plane ? ?	$\nu_{18}(e')$ $\nu_{10}(a'')$ $\nu_{10}(a'')$ B <sup>10</sup>
394 0 486 2				
675 6 755 0 864 2b 906 $\frac{1}{2}$	855 m 951 w, sh	$\nu_{15}(a')$ $\nu_{14}(a')$ $\nu_{13}(a')$ $\nu_{30}$ P branch	$\nu B-C$ ? $\rho CH_3$ $\rho CH_3$ $968 + \nu_i - \nu_i$	$\nu_6(a')$ $\nu_{21}(e'')$ $\nu_3(a')$ $\nu_9$ P branch
970 $\frac{1}{2}$	968 s 983 m	$\nu_{30}(a'')$ $\nu_{29}(a'')$ $\rho CH_3$	$\rho CH_3$	$\nu_9(a'')$ $675 + 320 = 995$
1060 $\frac{1}{2}$ 1145 6b	1149 vs 1162 vs	$\nu_{12}(a')$ $\nu_{28}(a'')$ $\rho CH_3$	Impurity? $\rho CH_3$	$\nu_{17}(e')$ $855 + 320 = 1175$
1195 0	1189 m 1300 sh		$855 + 336 = 1191$ $983 + 320 = 1303$ $968 + 336 = 1304$	
1295 1b 1440 2b	1309 vs 1459 m	$\nu_{11}(a')$ , $\nu_{27}(a'')$ $\nu_9(a')$ , $\nu_{10}(a')$ , $\nu_{26}(a'')$ $\nu_6(a')$ , $\nu_7(a')$ , $\nu_8(a')$ , $\nu_{23}(a'')$ , $\nu_{24}(a'')$ , $\nu_{25}(a'')$	$\nu BC$ $\delta CH_3$ $\delta CH_3$	$\nu_{16}(e')$ $\nu_3(a')$ , $\nu_4(a')$ , $\nu_{20}(e'')$ $\nu_8(a'')$ , $\nu_{14}(e')$ , $\nu_{15}(e')$
	1721 vw 1828 vw 1976 w 2167 w 2255 vw		$2 \times 855 = 1710$ $1149 + 675 = 1824$ $1309 + 675 = 1984$ $1309 + 855 = 2164$ $2921 - 675 = 2246$	
	2444 w 2456 w 2472 vw 2591 vw		$1459 + 983 = 2442$ $1309 + 1149 = 2458$ $1162 + 1309 = 2471$ $1149 + 1440 = 2589$	
2875 8b		$\nu_4(a')$ , $\nu_5(a')$	$\nu CH$	$\nu_2(a')$
2975 4b	2921 s 2986 s 3300 w 3522 w  3575 w 3729 w, sh 3853 w 4060 w 4144 w  4362 w 5798 w	$\nu_{22}(a'')$ $\nu_1(a')$ , $\nu_2(a')$ , $\nu_3(a')$ $\nu_{19}(a'')$ , $\nu_{20}(a'')$ , $\nu_{21}(a'')$	$\nu CH$ $\nu CH$ $\nu CH$ $2975 + 320 = 3295$ $2875 + 2 \times 320 = 3515$  $2921 + 2 \times 320 = 3561$ $855 + 2875 = 3730$ $968 + 2875 = 3843$ $1149 + 2921 = 4070$ $2986 + 1149 = 4135$ $2975 + 1162 = 4137$  $2921 + 1440 = 4361$ $2921 + 2875 = 5796$	$\nu_{13}(e')$ $\nu_1(a')$ , $\nu_{19}(e'')$ $\nu_7(a'')$ , $\nu_{12}(e')$

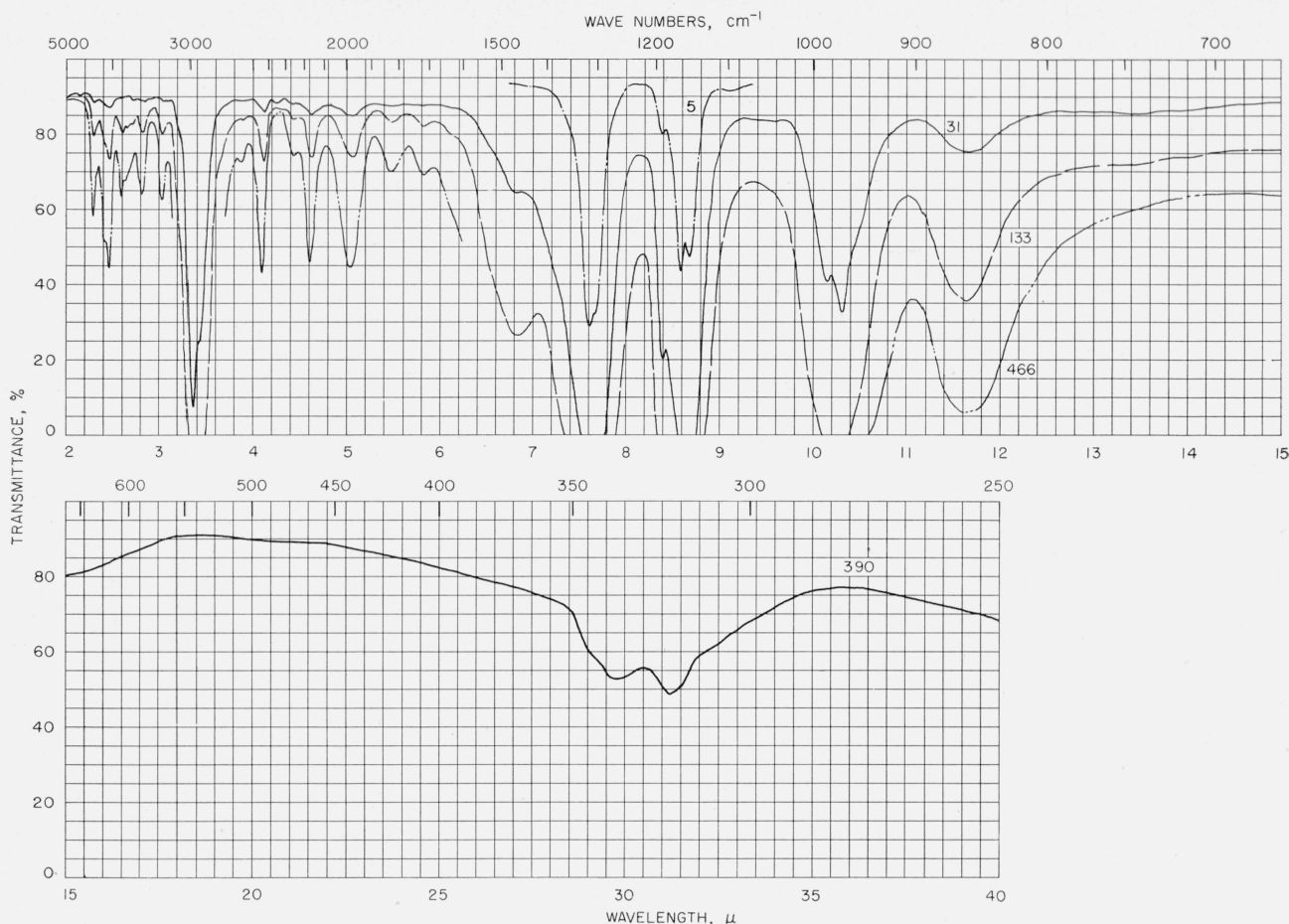


FIGURE 1. Infrared spectrum of gaseous trimethylborane,  $B(CH_3)_3$ .  
99.7 mole percent pure, 10-cm cell, pressures in millimeters of mercury.

#### 4. Structure, Vibrational Assignment, and Discussion

Electron diffraction studies [6] have shown trimethylborane to have a planar  $C_3B$  skeleton of symmetry  $D_{3h}$ . The configuration of the hydrogen atoms is not known. Barring completely free methyl group rotation, the molecule can be in one of the following symmetry classes:  $C_{3v}$  with one hydrogen from each methyl on one side of the  $C_3B$  plane and the remaining hydrogens on the other side;  $C_{3h}$  with one hydrogen from each methyl in the  $C_3B$  plane;  $C_3$  with the methyls rotated by an equal amount about their axes;  $C_s$  with a plane of symmetry containing the  $C_3$  axis of the  $C_3B$  skeleton; or  $C_1$  with no symmetry at all. The study of molecular models shows that the  $C_{3v}$  structure can probably be ruled out, whereas the  $C_{3h}$  structure is most attractive from steric considerations. The number of vibrations observed in the Raman effect but not in the infrared, and vice versa, is evidence against  $C_1$ ,  $C_3$ , and  $C_s$  symmetry, in which all transitions

are both Raman and infrared active. On the other hand, the abundance of vibrations observed in the 850 to 1,200  $cm^{-1}$  region makes the nondegenerate  $C_1$  or  $C_s$  symmetry more reasonable than the degenerate structures. In view of these considerations, both the  $C_s$  and the  $C_{3h}$  structures are treated, with the reservation that in the case of  $C_s$  symmetry the  $C_3B$  skeletal modes may behave as though they were in a molecule of  $D_{3h}$  symmetry because of weakness of methyl-skeleton interactions.

There are no assignments available for other boron-alkyl compounds to be used as a guide in the analysis of the trimethylborane spectrum. Sheppard and Simpson [7] have considered the effect of substituting fluorine for methyl groups in several paraffins and found good correlation between skeletal vibrations with usually little frequency shift for the unsymmetric vibrations and a moderate shift to higher frequencies for the symmetric vibrations of the fluorine analogs. This suggests that the vibrational assignment for  $BF_3$  can be used as an aid in assigning the skeletal modes of trimethylborane.

In order to demonstrate the extent of the reliability of this procedure, data for five pairs of compounds resembling  $\text{BF}_3$  and  $\text{B}(\text{CH}_3)_3$ , and not discussed by Sheppard and Simpson, are tabulated in table 2. The skeletal modes for acetone are assigned from the frequencies given by Price. All other assignments are those given by the original author. With the exception of the asymmetric stretching modes of  $\text{NF}_3$ , all vibrations are shifted to higher frequencies upon substitution of fluorine, some by quite large amounts. Of the two possible choices for the asymmetric stretching vibration for trimethylborane at 1,309 and 1,149  $\text{cm}^{-1}$ , 1,309  $\text{cm}^{-1}$  seems to be more probable by analogy with boron trifluoride. This is in disagreement with Siebert's choice of 1,149  $\text{cm}^{-1}$ .

The infrared spectra of a series of seven trialkyl boranes have been measured by Pickard, Dulaney, and Polly [8]. In addition, the infrared<sup>2</sup> and Raman [9] spectra of triethylborane have been measured at the Bureau. From these curves it is possible to select a satisfactory sequence of frequencies converging on 1,309  $\text{cm}^{-1}$  for trimethylborane for assignment to asymmetric skeletal stretching vibrations.

Intensity considerations supply further evidence concerning the assignment of the asymmetric stretching vibration. The band at 1,309  $\text{cm}^{-1}$  must include some contribution from the symmetric  $\text{CH}_3$  deformation modes. But it seems much too intense relative to the asymmetric  $\text{CH}_3$  deformation at 1,459  $\text{cm}^{-1}$  to be entirely due to  $\text{CH}_3$  vibrations. Hence another vibration must be superposed. Furthermore the great intensity of 1,145  $\text{cm}^{-1}$  in the Raman effect argues against its assignment to a nontotally symmetric mode. The corresponding vibration in the Raman spectrum of  $\text{BF}_3$  is not observed even though it is not a forbidden transition. On the other hand, no band is available in the neighborhood of 1,309  $\text{cm}^{-1}$  for assignment to the  $\text{B}^{10}$  isotopic molecule, whereas, 1,149  $\text{cm}^{-1}$  has such a neighbor of proper intensity at 1,189  $\text{cm}^{-1}$ .

Siebert's assignment of 486  $\text{cm}^{-1}$  to the  $\text{BC}_3$  out-of-plane bending vibration is satisfactory by analogy with the corresponding frequency in  $\text{BF}_3$ , but this vibration is Raman inactive and infrared active under the  $D_{3h}$  selection rules of  $\text{BF}_3$  (and also under  $C_{3v}$ ), whereas just the reverse activity is observed for the 486  $\text{cm}^{-1}$  band. Therefore, 336  $\text{cm}^{-1}$  is assigned to this vibration. The assignment of 320  $\text{cm}^{-1}$  to the in-plane deformation mode is natural and agrees with Siebert.

A choice must be made between the vibrations at 675 and 864  $\text{cm}^{-1}$  for assignment to the symmetric B—C stretching mode. 864  $\text{cm}^{-1}$  is perhaps in better agreement with the  $\text{BF}_3$  analogy, but its use would leave 675  $\text{cm}^{-1}$  unexplained, whereas 864  $\text{cm}^{-1}$  can be reasonably assigned to a methyl rocking mode. Furthermore, 675  $\text{cm}^{-1}$  is reported to be sharp and very strong in the Raman effect and is unobserved

TABLE 2. Skeletal vibration frequencies of fluoro and methyl compounds

Compound reference	Asymmetric stretch	Symmetric stretch	Out-of-plane bending	In-plane deformation
	$\text{cm}^{-1}$	$\text{cm}^{-1}$	$\text{cm}^{-1}$	$\text{cm}^{-1}$
$\text{NF}_3$ (a)	1,031	907	642	497
$\text{N}(\text{CH}_3)_3$ (b)	1,036	827	423	365
$\text{PF}_3$ (c)	892	860	487	344
$\text{P}(\text{CH}_3)_3$ (d)	708	653	305	263
$\text{AsF}_3$ (e)	707	644	341	274
$\text{As}(\text{CH}_3)_3$ (d)	583	568	239	223
$\text{O}=\text{CF}_2$ (f)	1,249	965	626	584
$\text{O}=\text{C}(\text{CH}_3)_2$ (g)	1,202	896	---	547
$\text{F}_2\text{C}=\text{CH}_2$ (h)	1,302	926	611	550
$(\text{CH}_3)_2\text{C}=\text{CH}_2$ (i)	986	800	391	378
$\text{BF}_3$ (i)	1,446	888	691	480
$\text{B}(\text{CH}_3)_3$	1,309	675	336	320

<sup>a</sup> E. L. Pace and Louis Pierce, J. Chem. Phys. **23**, 1248 (1955).

<sup>b</sup> K. W. F. Kohlrausch, Monatsh. **68**, 349 (1936).

<sup>c</sup> M. K. Wilson and S. R. Polo, J. Chem. Phys. **20**, 1716 (1952).

<sup>d</sup> E. J. Rosenbaum, D. J. Rubin, and C. R. Sandberg, J. Chem. Phys. **8**, 366 (1940).

<sup>e</sup> J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 630 (1934).

<sup>f</sup> A. H. Nielsen, T. G. Burke, P. J. H. Woltz, and E. A. Jones, J. Chem. Phys. **20**, 596 (1952).

<sup>g</sup> D. Price, J. Chem. Phys. **9**, 725 (1941).

<sup>h</sup> D. C. Smith, J. R. Nielsen, and H. H. Claassen, J. Chem. Phys. **18**, 326 (1950).

<sup>i</sup> J. E. Kilpatrick and K. S. Pitzer, J. Research NBS **38**, 191 (1947) RP1768.

<sup>j</sup> D. M. Gage and E. F. Barker, J. Chem. Phys. **7**, 455 (1939); D. M. Yost, D. DeVault, T. F. Anderson, and E. N. Lassette, J. Chem. Phys. **6**, 424 (1938).

in the infrared, whereas 864  $\text{cm}^{-1}$  is broad in the Raman effect and of medium intensity in the infrared spectrum. The assignment of 675  $\text{cm}^{-1}$  to the symmetric stretch is therefore preferred, in agreement with Siebert.

The skeletal force constants were calculated by treating the methyl groups as point masses [10]. The B—C stretching force constant  $f_{\text{BC}}$ , which depends on the asymmetric stretching frequency only, is found to be  $4.03 \times 10^5$  dynes/cm as compared with Siebert's value of  $3.64 \times 10^5$  dynes/cm. The self-consistency of the point-mass methyl treatment can be demonstrated by comparing the calculated value of  $(\nu_3^2 + \nu_4^2)$  with the experimentally determined value. Using Siebert's assignment, these numbers are  $1.57 \times 10^6$  and  $1.42 \times 10^6$   $\text{cm}^{-2}$ , respectively. The modified assignment proposed here gives  $1.62 \times 10^6$  and  $1.82 \times 10^6$ , respectively.

The methyl stretching and deformation modes are assigned in the usual way. Assuming a structure of  $C_s$  symmetry, the bands at 855, 906, and 1,149  $\text{cm}^{-1}$  are assigned to a' methyl rocking modes, and 968, 983, and 1,162  $\text{cm}^{-1}$  are assigned to a'' rocking modes. These bands are assigned in such a way that

<sup>2</sup> Unpublished curve obtained by the author.

where possible the  $a'$  transitions are most intense in the Raman effect and  $a''$  transitions are most intense in the infrared spectrum. Assuming a structure of  $C_{3h}$  symmetry, the methyl rocking modes are assigned as follows:  $a'$ -906,  $a''$ -968,  $e'$ -1,149,  $e''$ -864  $\text{cm}^{-1}$ , although 968 and 864  $\text{cm}^{-1}$  violate the selection rules. Raman lines at 394, 486, 755, and 1,060  $\text{cm}^{-1}$  remain unexplained. The 1,060  $\text{cm}^{-1}$  line might correspond to the impurity band observed near this frequency in the infrared spectrum. The lines at 486, 755, and 1,060  $\text{cm}^{-1}$  might arise from a methyl torsion vibration of frequency 160  $\text{cm}^{-1}$ :  $320+160=480$ ,  $906-160=746$ ,  $906+160=1,066$ . The shoulder at 345  $\text{cm}^{-1}$  in the infrared spectrum might result from a splitting of the skeletal deformation vibrations, or it might represent a  $B^{10}$  isotopic molecule vibration. The weak shoulder at about 960  $\text{cm}^{-1}$  in the infrared spectrum might be the  $P$  branch corresponding to 968  $\text{cm}^{-1}$ , or it might be an upper stage band  $968+\nu_1-\nu_1$ . In the assignment for the  $C_{3h}$  structure, the combination transitions assumed for the weak bands at 1,300, 2,444, 2,472, and 3,729  $\text{cm}^{-1}$  are in violation of selection rules, and the strong peaks at 983 and 1,162  $\text{cm}^{-1}$  are assigned to combination transitions.

## 5. Entropy and Methyl Rotation Barrier

Using observed vibration frequencies, moments of inertia  $I_A=I_B=112.92 \times 10^{-40}$  and  $I_C=209.02 \times 10^{-40}$   $\text{g}\cdot\text{cm}^2$ , and a reduced methyl moment of inertia of  $5.322 \times 10^{-40}$   $\text{g}\cdot\text{cm}^2$ , the contribution to the entropy at 199.92° K from translation, over-all rotation, internal free rotation, and vibration is 69.31  $\text{cal deg}^{-1}$  mole $^{-1}$  for the  $C_{3h}$  structure and 71.48  $\text{cal deg}^{-1}$  mole $^{-1}$  for the  $C_s$  structure. The difference is largely due to the difference in symmetry number of 81 for  $C_{3h}$  and 27 for  $C_s$ . Recently Furukawa and Park [11] determined the entropy of trimethylborane calorimetrically and found  $S_{199.92}=68.29$   $\text{cal deg}^{-1}$  mole $^{-1}$ . The difference of 0.34  $\text{cal deg}^{-1}$  mole $^{-1}$  per rotor for  $C_{3h}$  and 1.06  $\text{cal deg}^{-1}$  mole $^{-1}$  for  $C_s$  symmetry requires for agreement a sinusoidal barrier to free rotation of 750  $\text{cal/mole}$  or 1,640  $\text{cal/mole}$  for the  $C_{3h}$  and  $C_s$  structures, respectively.

## 6. Conclusion

In several respects the assignment for a trimethylborane structure of  $C_s$  symmetry is more satisfactory than the assignment for a  $C_{3h}$  structure.

Furthermore, the higher methyl rotation barrier associated with the  $C_s$  structure would seem more acceptable upon comparison with similar molecules, and indeed French and Rasmussen [12] predicted a barrier of 1,720  $\text{cal/mole}$  on empirical grounds. On the other hand, the nature of the barrier to rotation about a single bond and the role of methyl interactions in determining the barrier are not understood. Hence it is by no means clear that the use of standard methods for calculating the barrier is justified in the case of trimethylborane, or that the comparison of barriers between molecules is meaningful. Therefore, no conclusion is made regarding the correct structure of trimethylborane.

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