[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

The Raman Spectrum of Tetramethyldiborane. Apparatus for the Production of Raman Spectra at Low Temperatures

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An experimental procedure is described which simplifies the production of Raman spectra at low temperatures and in the absence of air. The Raman spectrum of liquid tetramethyldiborane at a temperature below 0° was photographed. No Raman lines with frequencies characteristic of terminal boron–hydrogen stretching were observed. This fact is evidence for a hydrogen-bridge-type structure in the tetramethyldiborane molecule and constitutes further evidence for the bridge structure in diborane. In the frequency range characteristic of bridge-hydrogen stretching two lines exist, instead of the one strong one found in the spectrum of B_2H_6.

A major factor contributing to the present interest in the spectra of boron compounds is the proposal of a hydrogen bridge structure for some of them.[2,3] Raman spectroscopy has been of limited value in the study of their structures because some of the compounds are very volatile, some are unstable at ordinary temperatures and some react vigorously with air. The purpose of this paper is to present a description of apparatus constructed for Raman investigations of highly reactive substances at low temperatures and to present the results of a study of tetramethyldiborane, $(CH_3)_4B_2H_2$.

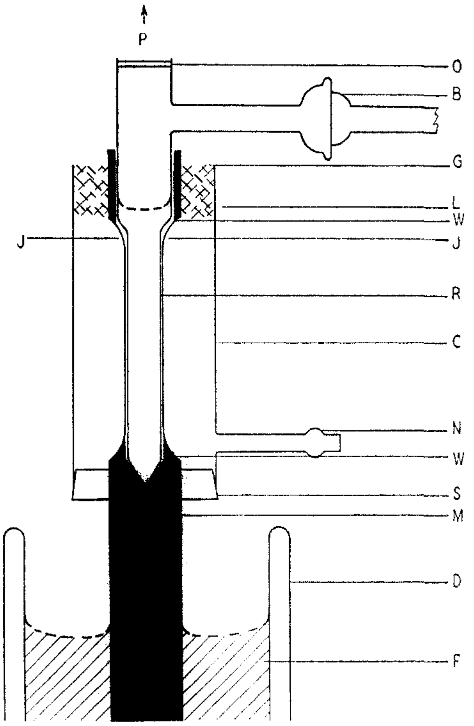
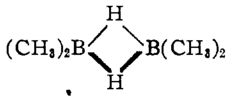


Fig. 1.—Diagrammatic cross section of Raman tube and cooling device: P, direction of right angle prism indicated by arrow; O, flat window; B, ball-and-socket ground joint; G, glass wool; L, liquid level; W, W, top and bottom of window cut into copper jacket; J, J, positions at which jets (not shown) might be placed; R, Raman tube; C, glass cylinder; N, inlet for dry nitrogen; S, cork stopper; M, solid portion of copper rod; D, dewar flask; F, coolant.

In none of the methyl derivatives of diborane, B_2H_6, which have been prepared have more than four of the hydrogen atoms been replaced by methyl groups.[4] Chemical evidence indicates that tetramethyl diborane has a symmetrical structure, *i.e.*, two methyl groups are attached to each of the boron atoms.[5] This fact suggests that if there is a bridge type of structure in diborane the four terminal hydrogen atoms have been replaced by methyl groups in tetramethyldiborane, thus



Evidence for or against this structure was to be expected in Raman and infrared spectra, but the substance decomposes above 0° and could not be studied until means were provided for maintenance of the liquid at a sufficiently low temperature and for purification of the compound just prior to its use.

Experimental

A sample of tetramethyldiborane was prepared for us by the method of Schlesinger and Walker,[4] in the Navy Inorganic Chemical Research Project, directed by Professor H. I. Schlesinger at the University of Chicago.[5] The sample was transferred to, and stored within one compartment of a glass vacuum system. The system was connected to a vertical Raman tube (Fig. 1) through a glass ball-and-socket joint which allowed sufficient movement to permit alignment of the tube with the spectrograph. Just before a Raman exposure was to be made, some of the liquid (about 3 cc.) was purified by bulb-to-bulb distillation and was then allowed to condense in the Raman vessel. When an exposure had been completed the sample was distilled back into the storage compartment.

During exposures the temperatures of the respective liquids were kept low by a heavy copper jacket which had been made from a copper rod about 2.5 centimeters in diameter. The upper end of the rod had been drilled to fit the Raman tube closely; the solid lower end was immersed in a suitable cooling medium. Temperature of the sample could be determined from its vapor pressure as indicated by a manometer built into the vacuum system. Adequate cooling of tetramethyldiborane was maintained with solid carbon dioxide and acetone. Lower temperatures for other substances have been obtained with liquid nitrogen. The level of the nitrogen in the dewar flask could be altered so as to establish and maintain the temperature required for each liquid.

Exciting light reached the Raman tube through two large windows cut into the copper jacket. The formation of interfering layers of condensed atmospheric moisture on the walls of the Raman vessel has been prevented by either of

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[2] H. C. Longuet-Higgins and R. P. Bell, *J. Chem. Soc.*, 250 (1943).

[3] K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945).

[4] H. I. Schlesinger and A. O. Walker, *ibid.*, **57**, 621 (1935).

[5] When our Raman work had been completed the sample was again distilled and handed to Dr. R. D. Cowan who used the same material in his investigations of the infrared spectrum of the compound.[6]

[6] R. D. Cowan, *J. Chem. Phys.*, **17**, 218 (1949).

two methods. The first utilized cold alcohol directed in two streams by glass jets (not shown in Fig. 1) against the exposed walls of the vessel and removed *via* a small trough mounted just below the windows of the cooling jacket. The other method employed a slow stream of nitrogen gas which flowed into the bottom of a glass cylinder (Fig. 1) and passed out through a layer of glass wool at the top.

For the work with tetramethyldiborane the first method, employing streams of alcohol, was used. The source of exciting light was a pair of General Electric H-11 lamps. The light was focused by two glass cylinders filled with a solution recommended by Edsall and Wilson,[7] as an optical filter. The filtered light consisted essentially of the 4358.3 Å. line and its relatively feeble neighbors, 4347.5 and 4339.2 Å. The spectrograph was a three-prism Steinheil instrument assembled with the collimator and camera lens of short focal length (f = 3.0). The slit width was 0.05 mm. and the time of exposure three hours. The plates were Eastman 103J spectrographic plates (antihalation-backed to reduce halation). Line frequencies were determined with a traveling microscope by comparison with the iron spectrum.

Results and Discussion

The frequencies (in cm.$^{-1}$) and the visually-estimated relative intensities of the lines observed in the Raman spectrum of tetramethyldiborane are shown in Table I. No lines were observed in the frequency range 2400 to 2700 cm.$^{-1}$. Since the frequencies associated with the stretching of the bond between a terminal hydrogen and a boron atom in diborane are near 2550 cm.$^{-1}$, we conclude—in agreement with Cowan[6]—that tetramethyldiborane contains no hydrogen atoms bonded in terminal positions to boron. The four highest frequencies arise, undoubtedly, from carbon–hydrogen modes of vibration. In the region, adjacent to the frequency 2102 cm.$^{-1}$, characteristic of the bridge-hydrogen in diborane,[8] no single line is outstanding; instead there are two relatively weak lines of 1987 cm.$^{-1}$ and 2137 cm.$^{-1}$. Existing data do not permit accurate comparisons of the intensities of lines of one compound with the intensities of those in the other. The absence of this and other information would render futile any present attempt to correlate these two frequencies with modes of vibration within the molecule. Whether the two lines are to be explained merely by the change in symmetry produced by the substitution of methyl groups for hydrogen, by Fermi resonance, or by some other factors, we do not know.

TABLE I

RAMAN SPECTRUM OF TETRAMETHYLDIBORANE

v = very, w = weak, m = medium, s = strong, b = broad

Line, cm.$^{-1}$	Intensity	Line	Intensity	Line	Intensity
		2137	w	844	m, b
2985	vs	1987	w	651	w
2952	vs	1445	s	516	vs
2885	m	1100	s, b	365	w
2841	m	1003	w	274	vw

The lines of lower frequencies cannot all be assigned to specific bonds or groups. A line of low frequency is apt to be associated with vibration of the molecule as a whole rather than with one of its constituent parts. The line of 516 cm.$^{-1}$, however, *seems* to be characteristic of the stretching of the boron–carbon bond. Its frequency differs but little from that, 495 cm.$^{-1}$, of a line which we have observed in the spectrum of trimethyl boron,[9] and have assigned to the symmetrical stretching vibration of the boron–carbon bond. Similarly the broad line, 844 cm.$^{-1}$, seems to be characteristic of the stretching of the boron–boron bond. It seems to be analogous to lines of similar frequencies, and similar assignments,[9] in diborane molecules incorporating ^{10}B and ^{11}B. The line 1445 cm.$^{-1}$ is probably associated with bond-bending vibrations in the methyl groups. We have not attempted to make assignments of the frequencies: 1100, 1003, 651, 365, and 274 cm.$^{-1}$. The argument for the bridge structure is not affected, of course, by the lack of explanations for these lines of lower frequencies.

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[7] J. T. Edsall and E. B. Wilson, *J. Chem. Phys.*, **6**, 124 (1938).

[8] A. N. Webb, J. T. Neu and K. S. Pitzer, *ibid.*, **17**, 1007 (1949).

[9] Not yet published.