chloride with the reactants in low concentration. Some examples of the induction period can be seen in Fig. 5.

The addition of benzoyl peroxide or molecular oxygen seems to have little effect on the induction period (Fig. 5). From the above experiment, it might be considered that the induction period was not produced from a radical reaction. It may be possible to interpret the induction period in terms of the time intervals required for the establishment of equilibria between toluene and halogen and their 1:1 complexes. But this is very unlikely because the complex formation seems to proceed very rapidly.[13]

Since retarding action of "unknown impurities" is also not impossible, we do not present any discussions on the nature of this induction period.

From the kinetic studies on the bromination of benzene without solvent and toluene in carbon tetrachloride, it was revealed that the rate of the reaction was proportional to $[RHBr_2][BrI]^3$ (RH = benzene or toluene) in either case. However, this does not mean that the above relation is always true in other cases.[14] More detailed studies on various effects upon the reaction rate or the induction period may afford a more distinct picture as to the reaction mechanism.

**Acknowledgment**.—The authors wish to express their sincere thanks to Professor Ryohei Oda for his suggestive discussions, and to Mr. Shiro Ohshima for assistance in the kinetic measurement.

[13] According to Benesi and Hildebrand,[11] "all solutions were freshly prepared directly before making absorption measurements." Their reproducible data of the spectra indicate the complex is formed very rapidly and the equilibrium is little shifted during the measurement.

[14] In the bromination of toluene in chloroform, *m* seems to be smaller than 3.

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# The Infrared Spectra of Stable Pentaborane and Deuterated Pentaborane

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Deuterated pentaborane was prepared by catalytic exchange between $B_5H_9$ and deuterium at room temperature. The infrared absorption spectra of gaseous $B_5H_9$ and $B_5D_9$ were obtained. Consideration of boron isotopic band structure and frequency shift on deuteration permits identification of the vibrational modes of several fundamentals. An assignment of the fundamental frequencies is given and the calculated entropy of gaseous $B_5H_9$ at 296°K. is compared to the experimental value. Characteristic vibrational frequencies of boranes are discussed.

The infrared and Raman spectra of stable pentaborane, $B_5H_9$, were first investigated by Taylor, *et al.*[1] Recently it has been shown that the pentaborane molecule has a $C_{4v}$ symmetry involving a boron skeleton in the form of a tetragonal pyramid.[2,3] One hydrogen atom is bound at each pyramidal apex, accounting for five of the hydrogens. Each of the four remaining hydrogen atoms is bound to the base of the pyramid in a position equidistant from the two nearest boron atoms, thus forming four of the unusual hydrogen "bridge" bonds characteristic of the boranes whose structures are known, $B_2H_6$ and $B_{10}H_{14}$. Since this structure has been established, it is possible to interpret these spectra in more detail. For this purpose completely deuterated pentaborane was prepared and the infrared spectra of $B_5H_9$ and $B_5D_9$ were examined.

## Experimental

Deuterated pentaborane was prepared by catalytic exchange between $B_5H_9$[4] and deuterium, using a chromia-alumina dehydrogenation catalyst (Harshaw No. CR-183). Before each exchange the catalyst was heated under vacuum at 450° for 24 hours. For each exchange, the gaseous mixture of deuterium and pentaborane in a mole ratio of at least 5-to-1 was connected to a receiving trap by a tube containing 5 g. of catalyst. With the catalyst at room temperature the receiving trap was cooled to 77°K. causing the pentaborane to diffuse through the catalyst chamber. The extent of deuteration was observed by periodic comparison of the relative absorptions in the infrared spectral regions where the B–H and B–D stretch motions are expected to occur (2600 and 1900 cm.$^{-1}$, respectively). Using deuterium of 99.5% purity and six exchanges, pentaborane was obtained in which more than 98.5% of the original hydrogen had been replaced by deuterium.[5]

Infrared spectra were obtained using a Perkin-Elmer model 21 spectrophotometer with NaCl prism for the spectral region 2100–650 cm.$^{-1}$, and a Perkin-Elmer model 12C with LiF and KBr prisms for the regions 4000–2100 and 650–400 cm.$^{-1}$, respectively. The spectra were studied using a 10.5-cm. cell with KBr windows sealed on with glyptal. Silicone lubricant was used in the stopcock. Spectral slit widths are shown on the spectra. Frequency accuracy is about ±2 cm.$^{-1}$ between 700 and 1500 cm.$^{-1}$ and decreases to ±5 cm.$^{-1}$ at 2500 cm.$^{-1}$ and at 400 cm.$^{-1}$. The purity of the $B_5H_9$ was periodically checked by measurement of the vapor pressure at 0°. The measured values always agreed within experimental error (±2 mm.) with the accepted vapor pressure (65.3 mm.).[6] Since the most probable decomposition reactions produce either $H_2$ or $B_2H_6$, the results indicate little decomposition. Additional indication of

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[1] W. J. Taylor, C. W. Beckett, J. Y. Tung, R. B. Holden and H. L. Johnston, *Phys. Rev.*, **74**, 234 (1950).

[2] (a) K. Hedberg, M. E. Jones and V. Schomaker, THIS JOURNAL, **73**, 3538 (1951); (b) W. J. Dulmage and W. N. Lipscomb, *ibid.*, **73**, 3539 (1951).

[3] H. J. Hrostowski, R. J. Myers and G. C. Pimentel, *J. Chem. Phys.*, **20**, 518 (1952).

[4] The $B_5H_9$ used in these studies was kindly supplied by Dr. A. E. Newkirk of the General Electric Company.

[5] No exchange was obtained in several preliminary experiments. (a) Deuterium and pentaborane show no exchange after 24 hours in the gas phase at 100°. (b) Increase of surface area using either glass wool or copper foil did not cause exchange in a deuterium-pentaborane mixture with a mole ratio of 5-to-1, a contact time of 15 hours, and the temperature at 100°. (c) Use of a molybdena–alumina catalyst at room temperature resulted in decomposition of pentaborane with production of other boranes including $B_2H_6$.

[6] H. L. Johnston, E. C. Kerr, J. T. Clarke and N. C. Hallett, Technical Report No. 6, ONR Project No. NR 058061, July 8, 1949.

purity is given by the absence of spectroscopic evidence of the other boranes for which reference spectra are available ($B_2H_6$, $B_4H_{10}$ and $B_{10}H_{14}$).

## Results

The spectrum of gaseous $B_5H_9$ is given in Fig. 1. It is in substantial agreement with that given by Taylor, *et al.*,[1] as shown in Table I, but with improved resolution of the $B^{10}$–$B^{11}$ isotopic structure. The spectrum of deuterated pentaborane was studied carefully after five exchanges and again after six exchanges. Although some decrease in intensity was noticeable in the region near 2600 cm.$^{-1}$ (the B–H stretch region), none of the prominent bands showed significant change in band shapes or relative intensities. Hence it is concluded that the prominent bands are due to completely deuterated pentaborane. Except for the very weak B–H stretch absorption, no bands due to $B_5D_8H$ could be identified. The spectrum of gaseous $B_5D_9$ is given in Fig. 2 and the observed bands are listed in Table II. The relative intensity of each band of $B_5H_9$ and $B_5D_9$ was estimated wher-

TABLE I

INFRARED AND RAMAN SPECTRA OF $B_5H_9$: FREQUENCY (CM.$^{-1}$) AND RELATIVE INTENSITY

| Infrared | | Raman |
|---|---|---|
| This research | Taylor, *et al.*[1] | Taylor, *et al.*[1] |
| | | 470 (vvw) |
| 568 (30) | 570 (m) | 566 (w,dp) |
| 605 (145) | 605[a] (vs) | 596 (w,dp) |
| 616 (225) | 619 (vs) | 606 (w,dp) |
| 625 (145) | 628 (vs) | |
| 648 (19) | | |
| 700 (6) | 702 (vw) | 700 (m,dp) |
| | | 738 (m,dp) |
| 793 (shoulder) | | 782 (m,dp) |
| 799[a] (19) | | 793 (s,p) |
| 807 (19.5) | | 803 (s,p) |
| 812 (13.5) | | |
| 816 (13) | | |
| 820 (12.5) | | |
| 882[a] (320) | | 884 (w,dp) |
| 890 (350) | | |
| 897 (406) | ~900 (vs), broad | |
| 918 (169) | | |
| 933 (100) | | |
| 985 (vvw) | | 982 (vs,p) |
| | | 999 (s,p) |
| 1034[a] (38) | 1035 (m) | |
| 1038 (38) | | |
| 1044 (42) | 1045 (m) | |
| 1081 (4) | | |
| 1126[a] (34) | 1125 (w) | 1120 (m,p) |
| 1144 (16) | 1143 (vw) | |
| 1186[a] (4) | 1187 (vw) | 1170 (vw,p) |
| 1191 (4) | | 1193 (vw,p) |
| 1195 (7) | | |
| 1228[a] (4) | 1210 (vw) | |
| 1232 (3) | 1230 (vw) | |
| 1349[a] (14) | | 1350 (vw) |
| 1310–1360 (24) broad | | 1387 (vw) |
| 1402 (275) | | |
| 1413[a] (488) | ~1415 (vs) broad | |
| 1430 (388) | | 1440 (vw) |
| 1449[a] (351) | | |
| 1464 (225) | | |
| 1488[a] (135) | | |
| 1496 (141) | 1500 (w) | |
| 1504 (138) | | |
| 1513 (65) | | |
| 1574 (19) | | |
| 1621[a] (43) | 1620 (m) | |
| 1635 (44) | | |
| 1641 (38) | | |
| 1725[a] (24) | | |
| 1736 (22) | | 1740–1840 (w,dp) |
| 1802[a] (125) | | |
| 1844[a] (80) | | 1840 (m,p) |
| 1912[a] (22) | | 1870–2300 |
| 1922 (22) | | ~10 vw lines |
| 1966[a] (20) | | |
| 2110 (10) | | 2077 (w,p) |
| 2170 (9) | | 2152 (w,p) |
| 2245 (9) | | |
| 2460 (8) | | |
| 2598 (1270) | | 2600 (vs,dp) |
| 2610 (1130) | | |
| 3070 (8) | | |
| 3200 (8) | | |
| 3285 (4) | | |

[a] Frequency considered to be due to the species $B_5{}^{11}H_9$.

TABLE II

INFRARED SPECTRUM OF GASEOUS $B_5D_9$ (CM.$^{-1}$)

| | | | |
|---|---|---|---|
| 430[a] | (130) | 1046 (sh) | (280) |
| 442[a] | (140) | 1056[a] | (625) |
| 639[a] | (62) | 1068 | (360) |
| 648 | (64) | 1110 (sh) | (30) |
| 668[a] | (5) | 1180[a] | (35) |
| 673 | (2) | 1186 | (37) |
| 732 (sh) | (210) | 1198 | (33) |
| 740[a] | (430) | 1230 | (4) |
| 743 | (420) | 1292[a]–1300 | (77) |
| 746 | (390) | 1338[a] | (101) |
| 749 | (380) | 1342 | (98) |
| 752 | (360) | 1347 | (84) |
| 761 | (280) | 1377 | (51) |
| 771 | (220) | 1386[a] | (53) |
| 779 | (160) | 1397 | (55) |
| 795 | (30) | 1420 (broad) | (40) |
| 842[a] | (18) | 1520 (broad) | (14) |
| 849 | (19) | 1780 (broad) | (3) |
| 856 | (20) | 1962 | (840) |
| 874 | (9) | 1972 | (710) |
| 946 (sh) | (8) | 1989 | (150) |
| 960[a] | (17) | 2005 | (130) |
| 964 | (16) | 2100 | (3) |
| 968 | (14) | | |
| 972–980 | (15) | | |
| | | 2180 | (3) |
| | | 2235 | (3) |
| | | 2370 | (6) |
| | | 2520 | (3) |
| | | 2600 | (10) |

[a] Frequency assigned to the species $B_5{}^{11}D_9$.

ever possible from at least one spectrum in which that band showed 20 to 70% absorption. The relative intensities given parenthetically in Tables I and II were obtained by dividing the value of $\log_{10} I_0/I$ at the frequency of maximum absorption by the cell length (10.5 cm.) and by the pentaborane pressure in millimeters and multiplying by $10^5$.

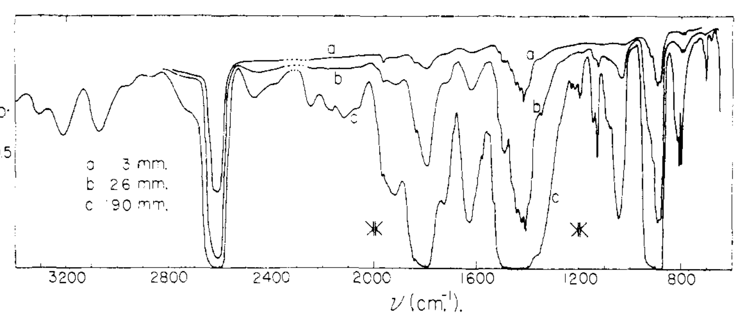

Fig. 1a.—Infrared spectrum of gaseous $B_5H_9$ (NaCl prism).

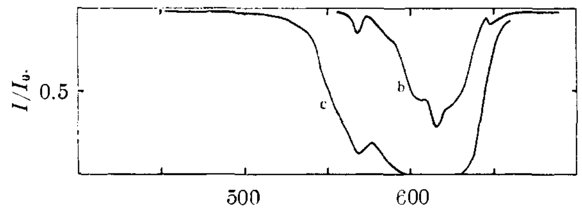

Fig. 1b.—Infrared spectrum of gaseous $B_5H_9$ (KBr prism).

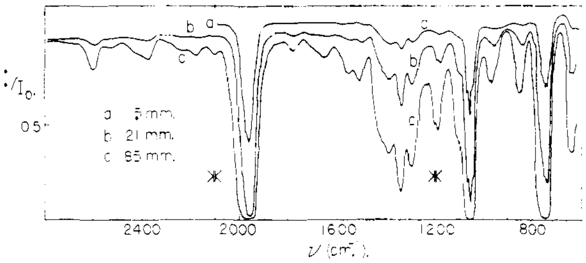

Fig. 2a.—Infrared spectrum of gaseous $B_5D_9$ (NaCl prism).

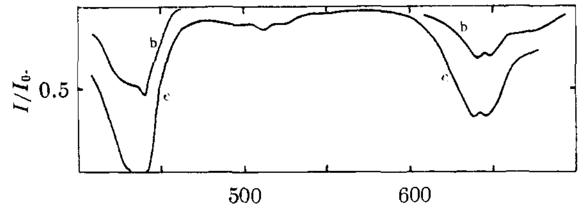

Fig. 2b.—Infrared spectrum of gaseous $B_5D_9$ (KBr prism).

## Discussion

The selection rules and distribution of fundamental frequencies appropriate to $C_{4v}$ symmetry are given in Table III. As pointed out by Taylor, *et al.*, the number of polarized lines observed in the Raman spectrum of pentaborane exceeds the number appropriate to $C_{4v}$ symmetry (note that inspection of the symmetry coördinates indicates that two $A_1$ fundamentals are expected in the BH stretch region near 2600 cm.$^{-1}$, superimposed upon one E type motion which accounts for the Raman depolarization, in addition to the ten lines observed to be polarized). The infrared spectrum indicates that some of these lines are associated with different isotopic species of $B_5H_9$. The calculated abundances of several of the isotopic species are presented in Table IV, calculated with assumed abundances of $B^{10}$ and $B^{11}$ of 18.83 and 81.17%, respectively. Each species is described and its molecular symmetry given. The qualitative influence of substitution of $B^{10}$ for $B^{11}$ atoms is to shift the fundamental to a higher frequency. Assuming that the intensity is determined mainly by the abundance of the species, the relative intensities may be estimated from the relative abundances. These are given in the last column of Table IV. In this approximation, the fundamental frequencies which involve significant skeletal motion should have a characteristic band structure consisting of two absorptions of about equal intensity on the low frequency side of the band, and successively weaker absorptions extending to higher frequencies. This band structure was found for several bands, as shown in Figs. 3 and 4. Several other bands showed the appropriate general band contour, steep on the low frequency side and sloping off on the high frequency side.

TABLE III

SELECTION RULES AND DISTRIBUTION OF FUNDAMENTAL FREQUENCIES FOR PENTABORANE

| Class | Activity[a] | Number of fundamentals Skeletal | Total |
|---|---|---|---|
| $A_1$ | R, IR | 2 | 7 |
| $A_2$ | Inactive | 0 | 2 |
| $B_1$ | R | 2 | 5 |
| $B_2$ | R | 1 | 4 |
| E | R, IR | 2 | 9 |

[a] R = Raman active; IR = infrared active.

TABLE IV

ABUNDANCES AND SYMMETRIES OF SOME OF THE ISOTOPIC SPECIES OF PENTABORANE

| No. | Species | Symmetry | Description | Abundance | Relative abundance |
|---|---|---|---|---|---|
| 1 | $B_5{}^{11}H_9$ | $C_{4v}$ | | 0.344 | (1.00) |
| 2 | $B_4{}^{11}B^{10}H_9$ | $C_s$ | $B^{10}$ in ring | .336 | 0.98 |
| 2′ | | $C_{4v}$ | $B^{10}$ at apex | .084 | .24 |
| 3 | $B_3{}^{11}B_2{}^{10}H_9$ | $C_s$ | $B^{10}$ in ring, apex | .077 | .22 |
| 3′ | | $C_s$ | $B^{10}$ in ring, adjacent | .077 | .22 |
| 3″ | | $C_{2v}$ | $B^{10}$ in ring, opposite | .038 | .11 |
| 4 | $B_2{}^{11}B_3{}^{10}H_9$ | $C_s$ | $B^{11}$ in ring, apex | .016 | .05 |
| 4′ | | $C_s$ | $B^{11}$ in ring, adjacent | .016 | .05 |
| 4″ | | $C_{2v}$ | $B^{11}$ in ring, opposite | .008 | .02 |

The quantitative boron isotopic shift may be roughly estimated using the product rule. For example, the species 2 in Table IV is of symmetry $C_s$ and the product rule indicates for $B_5H_9$ that the shift of the frequency product in the totally symmetric class, A′, will be 1.070. This shift may be assumed to be concentrated mainly in the skeletal motions, giving a reasonable estimate of the frequency shifts for individual vibrations. This type of calculation indicates that the infrared active skeletal motions of species 2 should shift by a factor

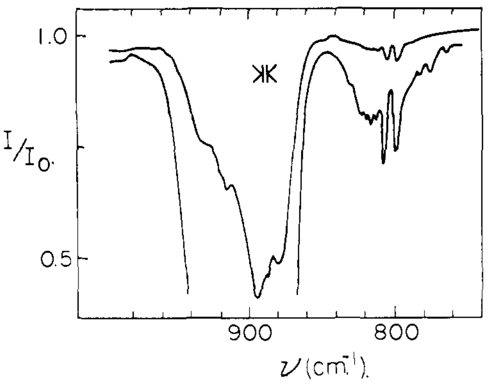

Fig. 3.—Boron isotopic band structure: $B_5H_9$.

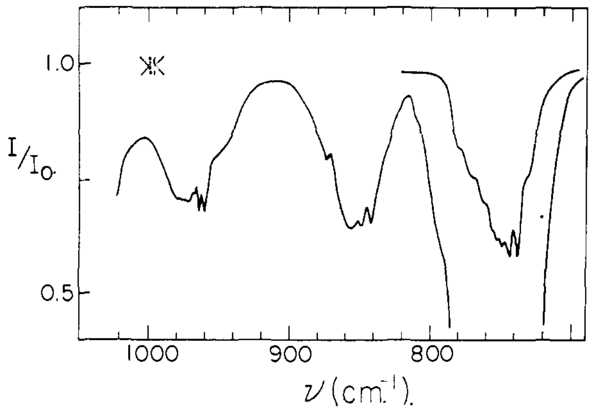

Fig. 4.—Boron isotopic band structure: $B_5D_9$.

averaging about 1.011. The spacings of the two most prominent absorptions in the two $B_5H_9$ bands in Fig. 3 are in rough agreement with this figure: 807/799 = 1.010 and 897/882 = 1.017.

The band contours may be further complicated by resolution of the PQR envelope of the rotational fine structure. Using the methods of Gerhard and Dennison,[7] the separations between maximum absorptions of the P and Q branches (or Q and R branches) of parallel bands ($A_1$) were calculated to be 14.4 and 12.4 cm.$^{-1}$ for $B_5H_9$ and $B_5D_9$, respectively. For perpendicular bands (E), the spacings were calculated to be 11.8 and 10.1. Evidence of rotational band contour is suggested in a few bands by the presence of a shoulder on the low frequency side, interpreted to be the P branch of the band due to species 1. Since the presence of this feature is characteristic of parallel bands, aid is obtained in the identification of totally symmetric motions. Bands which show evidence of this P branch are the following: $B_5H_9$, 1413 cm.$^{-1}$; $B_5D_9$, 1056, 960, 740. The $B_5D_9$ band at 1056 cm.$^{-1}$ has a band contour very close to that expected for a parallel band. This band is shown in Fig. 5 superimposed on the $B_5H_9$ band at 1413 cm.$^{-1}$. The similarity in band structures and intensities makes this association seem certain. The spacings observed between the low frequency shoulder and band center are 11 and 10 cm.$^{-1}$ for the 1413 and 1056 cm.$^{-1}$ bands, respectively. The absence of boron isotopic structure is presumably explained by the isotopic shift on deuteration, 1.34, indicating very little skeletal motion in this vibrational mode. The difficulty with assignment of these bands as $A_1$ (parallel) fundamental frequencies is that the 1413 cm.$^{-1}$ band is the second most intense band in the infrared spectrum but is not observed in the Raman spectrum of $B_5H_9$. This is in contrast to other $A_1$ fundamentals. Excluding the overlapping lines at 2600 cm.$^{-1}$, the most intense lines in the Raman spectrum are polarized, hence $A_1$, and the corresponding infrared bands are weak. Assuming the assignment of this frequency to the $A_1$ class, it is probably largely symmetrical B–H bending of the basal hydrogens. This would give a large dipole change (and high infrared intensity) if the basal B–H bonds have significant bond moments. The low Raman intensity must, then, be explained on the assumption that the polarizability change associated with this non-skeletal motion is low. The $B_5D_9$ band at 740 cm.$^{-1}$ shows a low frequency shoulder at 732 cm.$^{-1}$. However, the association of this band with the $B_5H_9$ band at 882 cm.$^{-1}$ is very certain and since the Raman absorption at 884 has been observed to be depolarized, it is not assigned to the $A_1$ class.

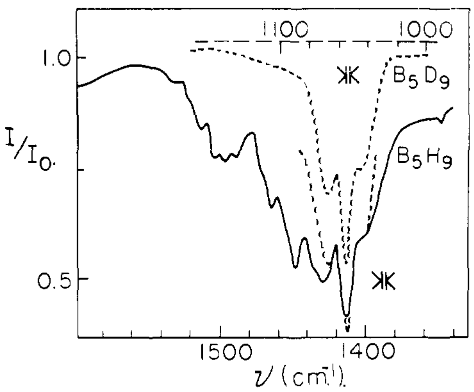

Fig. 5.—Comparison of band contours of the $B_5H_9$ band at 1413 cm.$^{-1}$ and the $B_5D_9$ band at 1056 cm.$^{-1}$.

Using frequency shifts on deuteration, intensities and band shapes, it is possible to associate many of the bands of $B_5H_9$ with bands of $B_5D_9$. The $B_5H_9$–$B_5D_9$ correlations 2598–1962, 1802–1386, 882–740 and 799[8]–639 cm.$^{-1}$ are easily obtained. As mentioned above. the 1413–1056 cm.$^{-1}$ correlation seems quite certain and this association indicates that more than one $B_5H_9$ vibration absorbs in the 1400–1500 cm.$^{-1}$ region. The remaining correlations, given in Table V, seem the most reasonable on the basis of considerations of band contours, intensities and isotopic shift on deuteration.

The polarization of coincident Raman lines identifies the following infrared bands of $B_5H_9$ as $A_1$ frequencies: 799, 985, 1126, 1844, 1186, 2110 (2077) and 2170 (2152) cm.$^{-1}$. On the basis of intensity in the Raman spectrum, the first four were selected as fundamental frequencies. The very weak band at 1186 cm.$^{-1}$ is assigned as the harmonic of the band at 605 cm.$^{-1}$. Two additional totally symmetric B–H stretching frequencies must

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

(8) Where boron isotopic structure is evidenced in a band, the band is henceforth identified by the frequency considered to correspond to the $B_5{}^{11}H_9$ species.

TABLE V

CORRELATION OF $B_5H_9$ AND $B_5D_9$ BANDS

| $B_5H_9$ |  | $B_5D_9$ |  | $\frac{\nu B_5H_9}{\nu B_5D_9}$ |
|---|---|---|---|---|
| Frequency | Intensity | Frequency | Intensity |  |
| 2598 | 1270 | 1962 | 840 | 1.32 |
| 1802 | 125 | 1386 | 53 | 1.30 |
| 1413 | 488 | 1056 | 625 | 1.34 |
| 882 | 320 | 740 | 430 | 1.19 |
| 799 | 19 | 639 | 62 | 1.25 |
| 1966 | 20 | 1520 | 14 | 1.29 |
| 1621 | 43 | 1292 | 77 | 1.25 |
| 1449 | 351 | 1180 | 35 | 1.23 |
| 1126 | 34 | 960 | 17 | 1.17 |
| 1034 | 38 | 842 | 18 | 1.23 |
| 605 | 145 | 442 | 140 | 1.37 |
| 568 | 30 | 430 | 130 | 1.32 |

occur in the region near 2600 cm.$^{-1}$. The remaining fundamental in this class is selected at 1413 cm.$^{-1}$ on the basis of the band contour (see Fig. 5). The absorption in the region 1800–2000 cm.$^{-1}$ seems to be associated with the B–H* stretch,[9] and hence there should be only one totally symmetric motion here. The band at 1844 cm.$^{-1}$ is assigned as the totally symmetric bridge hydrogen stretch. The boron isotopic structures of the bands at 799 and 1126 cm.$^{-1}$ indicate that the corresponding motions involve considerable skeletal movement. Keller and Johnson[10] discuss the absence of a symmetrical skeletal motion at lower frequency. These skeletal motions must each involve a considerable amount of B–B stretch since the symmetrical apical angle bend necessitates change of the boron distances.

The frequencies of the doubly degenerate E class appear as coincidences of infrared bands and depolarized Raman lines. Such coincidences are found at 568, 605, 700, 882, 1349, 1449, 1802 and 2598 cm.$^{-1}$. These were assigned as fundamentals except for the band at 1349 cm.$^{-1}$ which is very weak in both the infrared and the Raman spectra. Two additional fundamental frequencies of the E class must be selected from the remaining unassigned infrared bands. The bands remaining, in order of decreasing intensities, are 1488 (135), 1621 (43), 1034 (38), 1966 (20), 2245 (9), 1081 (4), 1228 (4) and 668 cm.$^{-1}$ (vvw). The bands at 1034 and 1621 cm.$^{-1}$ have been selected as fundamentals. The intensity of the discarded band at 1488 cm.$^{-1}$ is in part caused by overlap with the band at 1449 cm.$^{-1}$.

Several lines are observed in the Raman spectrum of $B_5H_9$ which are not observed in the infrared spectrum. The Raman lines observed at 470, 738, 782, 1387 and 1870 cm.$^{-1}$ are assigned to the classes $B_1$ and $B_2$, giving a partial assignment.

Table VI lists the frequencies assigned as fundamentals for $B_5H_9$ and their classification according to symmetry type. The frequencies parenthetically enclosed are estimated. The $B_5D_9$ band at 1420 cm.$^{-1}$ was estimated from the deuteration shift of the 1802 cm.$^{-1}$ band of $B_5H_9$. The remaining totally symmetric mode of $B_5D_9$ was calculated to be 835 cm.$^{-1}$ using the product rule.[11] This band is presumably very weak in the infrared spectrum and strong in the Raman spectrum as is the $B_5H_9$ band at 985 cm.$^{-1}$. The E class fundamental at 540 cm.$^{-1}$ was similarly calculated using the product rule. All other estimated frequencies were guessed after consideration of the probable vibrational modes.

TABLE VI

CLASSIFICATION OF $B_5H_9$ AND $B_5D_9$ FREQUENCIES (CM.$^{-1}$)

| Class. | $B_5H_9$ | $B_5D_9$ |
|---|---|---|
| $A_1$ | 799 | 639 |
|  | 985 | (835)[a] |
|  | 1126 | 960 |
|  | 1413 | 1056 |
|  | 1844 | (1420)[b] |
|  | 2600 | 1960 |
|  | 2600 | 1960 |
| E | 568 | 430 |
|  | 605 | 442 |
|  | 700 | (540)[a] |
|  | 882 | 740 |
|  | 1034 | 842 |
|  | 1449 | 1180 |
|  | 1621 | 1292 |
|  | 1802 | 1386 |
|  | 2598 | 1962 |
| $B_1$ | 782 | .. |
|  | (900)[b] | .. |
|  | 1387 | .. |
|  | 1870 | .. |
| $B_2$ | 470 | .. |
|  | (1100)[b] | .. |
|  | (1500)[b] | .. |
|  | 738 | .. |
|  | 2600 | .. |
| $A_2$ | (500)[b] | .. |
|  | (1450)[b] | .. |

[a] Not observed; calculated using product rule. [b] Not observed; estimated.

**Characteristic Borane Frequencies.**—With the present assignment it is possible to review the assignment of characteristic borane frequencies in the infrared. The complete assignment of $B_2H_6$[12] and the Raman spectrum of $B_2H_2(CH_3)_4$[13] are useful in this regard. These frequencies are indicated in Table VII.

The absorption in the region 2500–2600 cm.$^{-1}$ is characteristic of the B–H or B–$H_2$ stretching frequencies and can be used to verify the presence of non-bridge hydrogens. The absorption in the region 1800–2140 cm.$^{-1}$ is characteristic of the B–H* stretching frequencies and can be used to verify the presence of bridge hydrogens. The corresponding bands of decaborane are near 1900 cm.$^{-1}$, suggesting that the "half-bridge" hydrogens of $B_5H_9$ and $B_{10}H_{14}$ have a somewhat lower stretching force constant than the bridge hydrogens of diborane. Bridge connected boron atoms show a

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(9) The bridge hydrogen atoms are distinguished by the symbol H*.

(10) W. E. Keller and H. L. Johnston, *J. Chem. Phys.*, **20**, 1749 (1952).

(11) The calculated values of $\pi_i\nu_i(B_5H_9)/\pi_i\nu_i(B_5D_9)$ using the moments of inertia determined by Hrostowski and Myers (see ref. 14) are: $A_1$, 5.295; E, 9.135.

(12) R. C. Lord and E. Nielsen, *J. Chem. Phys.*, **19**, 1 (1951).

(13) B. Rice, J. M. Gonzalez Barredo and T. F. Young, THIS JOURNAL, **73**, 2306 (1951)

TABLE VII

CHARACTERISTIC FREQUENCIES OF BORANES

| Motion | $B_2H_6$[11] | $B_2H_2(CH_3)_4$[12] | $B_5H_9$ |
|---|---|---|---|
| $BH_2$ stretch | 2610 | .. | .. |
| | 2520 | .. | 2610 |
| BH stretch | .. | .. | 2598 |
| | 2102 | 2137 | 1844 |
| BH* stretch | 1982 | 1987 | 1802 |
| | 1847 | | |
| | 1180 | | |
| | 1173 | | |
| $BH_2$ bend | 1010 | .. | .. |
| | 970 | | |
| | | | 1621 |
| BH bend | .. | .. | 1449 |
| | | | 1413 |
| B–B stretch | .. | .. | 1126 |
| $BH^*_2B$ stretch | 799 | 844 | 799 |
| BH* bend | 370 | 365 | 605 |
| | | | 568 |

stretching frequency near 800 cm.$^{-1}$ which exhibits considerable boron isotopic structure and for $B_5H_9$ shifts on deuteration by a factor around 1.25.

The low frequency bands of $B_5H_9$ at 568 and 605 cm.$^{-1}$ show unexpectedly large isotopic shifts on deuteration. It is interesting that there is a corresponding mode of $B_2H_6$ at 370 cm.$^{-1}$ which shifts by a factor close to $\sqrt{2}$ on deuteration. These bands must correspond to bridge hydrogen motions and they provide the basis for the estimate of the frequency of one of the $A_2$ vibrational modes of $B_5H_9$ at 500 cm.$^{-1}$.

**Thermodynamic Properties of Pentaborane.**—Since several fundamental vibrations were selected only by consideration of expected vibrational type, it does not seem appropriate to include detailed calculations of thermodynamic functions. However, the entropy of gaseous $B_5H_9$ at 296°K., measured by Johnston, Kerr, Clarke and Hallett[6] together with the accurate values of the moments of inertia from the microwave studies[3,14] provide one check upon the present assignment. The calculated entropy of $B_5H_9$ at 296°K., 65.73 cal./deg. mole, may be compared to the experimental value, 65.75 cal./deg. mole.[6] This agreement is fortuitous since the uncertainty in each of the numbers is of the order of a few tenths of an entropy unit (the experimental entropy includes a −2.68 cal/deg. mole ideal gas correction based upon Berthelot's equation) but it probably does substantiate the conclusion that there is one unobserved, low frequency fundamental (assigned here as an $A_2$ mode at about 500 cm.$^{-1}$).

[14] A report by H. J. Hrostowski and R. Myers on the microwave study of $B_5H_9$ and $B_5D_9$ is in press (*J. Chem. Phys.*). They give the product of the principal moments of inertia for $B_5^{11}H_9$, $2.460 \times 10^{-114}$ g.$^3$cm.$^6$.

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# Dipole Moments and Absorption Spectra of *o*-Benzoquinone and its Related Substances

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Dipole moments of *o*-benzoquinone and 1,2-naphthoquinone were determined in benzene solutions as 5.1 and 5.67 *D*, respectively. These high moments can be explained on the basis of the $\pi$-electron distribution calculated by the molecular orbital method. The solvent effects on the electronic absorptions were measured with *o*-, *p*-benzoquinone, 1,2- and 1,4-naphthoquinone. As a result of the measurement, it was found that the absorptions of these quinones appearing in the visible region shift to the side of shorter wave lengths with the increasing dielectric constant of the solvent. This probably shows that these absorptions are due to the $n$-$\pi^*$-transition.

It is known that quinones have many interesting properties. They absorb visible light; they form a group of molecular compounds[1]; their oxidation–reduction potentials are generally high and positive[2]; further, a certain quinone has an abnormally high dipole moment.[3] Of these properties oxidation–reduction potential appears to be an unique example of being fully studied; *viz.*, Evans, *et al.*,[2] have discussed this property in detail with reference to $\pi$-electrons.

The work in the present paper was undertaken to study the problem somewhat in a wider scope. First, the dipole moments and visible and near ultraviolet absorption spectra measured for several quinones will be reported. Second, the experimental result on the dipole moment will be compared with the theoretical value obtained by the use of the molecular orbital method.

## Experimental

**Materials.**—*o*-Benzoquinone[4] was prepared by oxidation of catechol and recrystallized from ether. The dark-red crystalline product melted at 60–70° with decomposition.

*p*-Benzoquinone was prepared by oxidation of commercial hydroquinone and purified by repeated sublimation, m.p. 116°.

1,4-Naphthoquinone[5] was obtained by oxidation of 1,4-

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[1] P. Pfeiffer, "Organische Molekülverbindungen," Ferdinand Enke, Stuttgart, 1927; G. Weiss, *J. Chem. Soc.*, 245 (1942), and 462 (1943); H. M. Powell, G. Huse and P. M. Cooke, *ibid.*, 153 (1943), and 435 (1943); L. Michaelis and S. Granick, THIS JOURNAL, **66**, 1023 (1944).

[2] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 303; E. Berliner, THIS JOURNAL, **68**, 49 (1946); M. G. Evans, *Trans. Faraday Soc.*, **42**, 113 (1946); M. G. Evans, J. Gergely and J. de Heer, *ibid.*, **45**, 312 (1949).

[3] C. C. Caldwell and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1614 (1939). The dipole moment of phenanthrenequinone was determined by them as 5.6 *D*.

[4] R. Willstätter and A. Pfannenstiel, *Ber.*, **41**, 2580 (1908); S. Goldschmidt and F. Graef, *ibid.*, **61**, 1858 (1928); R. Kuhn and I. Hammer, *ibid.*, **83**, 413 (1950). *o*-Benzoquinone is unstable, so the measurement with this substance has been made within six hours after preparation.

[5] *Org. Syntheses*, **17**, 4, 24 (1937).