Absorption Spectrum of Borazole in the Vacuum Ultraviolet

J. R. Platt, H. B. Klevens, and G. W. Schaeffer

Articles you may be interested in

Absorption Spectrum of Borazole in the Vacuum Ultraviolet

J. R. PLATT

Physics Department, University of Chicago, Chicago, Illinois

H. B. KLEVENS* AND G. W. SCHAEFFER

Chemistry Department, University of Chicago, Chicago, Illinois

The absorption spectra of triborine-triamine or borazole, $B_3N_3H_6$, has been studied with a fluorite vacuum spectrograph in the region 2250–1700A in *n*-heptane solution. The compound was prepared by the reaction between diborane and ammonia.

Four diffuse bands are found, starting at 1995A, with spacing about 900 cm^{-1}. These seem analogous to the 2000A bands of benzene, but the intensity is about 10 times smaller. A strong continuum, like the 1800A benzene peak, has its maximum at 1720A or below. No bands like the benzene 2600A group were found, though they would have been seen if their intensities had been only 1/20th that of the latter.

The spectrum of a boron hydride, B_5H_9, has also been obtained but shows only a featureless continuum in this wave-length region.

INTRODUCTION

THE absorption spectra of triborine-triamine or borazole, $B_3N_3H_6$, and of a boron hydride, B_5H_9, have been studied in the region 2250–1700A. The compounds were studied in *n*-heptane solution in an 0.13-mm cell.

The borazole spectrum is much like that of benzene. This similarity is reasonable from the resemblances between the electronic structures in the two compounds. Borazole, which is iso-electronic with benzene, exhibits properties so similar to that compound that it has frequently been called "inorganic benzene." On the basis of chemical properties,[1,2] electron diffraction,[3] isomer number,[4] and infra-red and Raman

(two forms)

spectra,[5] the compound has been demonstrated to have a ring structure analogous to benzene. Resonance between structure I and the two equivalent structures of type II is probably adequate to describe the molecule.[1] The contribution of structures II is evident from the decrease in the $B-N$ bond distance which is 1.44A for borazole compared with 1.62A for the simple $B-N$ bond as observed in trimethylaminoborine.[6]

APPARATUS AND TECHNIQUE

The Cario-Schmitt-Ott fluorite vacuum spectrograph used in the present work was kindly loaned to us by the University of Michigan. Absolute intensities were measured by methods like those described earlier.[7] However, the sector-rotor used before for photometric calibration was not available, and the calibration was performed by use of timed exposures, the correction for reciprocity failure being obtained with the help of calibrated screens. Below 1800A, where the light source is relatively weak, it was necessary to make a correction for scattering in the spectrograph, and the absolute values are less reliable in this region. The correction was estimated by extrapolation from measurements of the scattered background light below 1700A
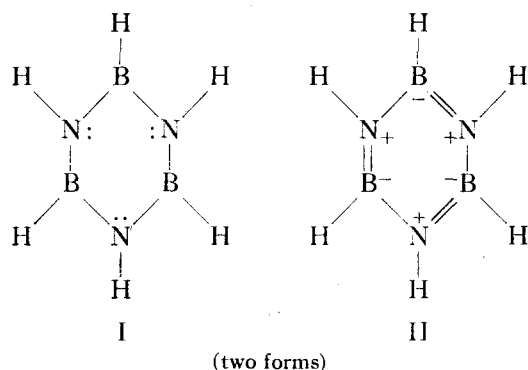
* Present address: Research Laboratories, the Firestone Tire & Rubber Company, Akron, Ohio.
[1] E. Wiberg and A. Bloz, Berichte **73**, 209 (1940).
[2] A. Stock and E. Pohland, Berichte **59**, 2215 (1926).
[3] S. H. Bauer, J. Am. Chem. Soc. **60**, 524 (1938).
[4] H. I. Schlesinger, L. Horwitz, and A. R. Burg, J. Am. Chem. Soc. **58**, 409 (1936).
[5] B. L. Crawford, Jr. and J. T. Edsall, J. Chem. Phys. **7**, 223 (1939).
[6] S. H. Bauer, J. Am. Chem. Soc. **59**, 1804 (1937).
[7] J. R. Platt, I. Rusoff, and H. B. Klevens, J. Chem. Phys. **11**, 535 (1943).

where the *n*-heptane solutions are known to be completely opaque.

Extinctions computed from different plates are consistent to ±20 percent, and the mean values given here are believed to be accurate to the same figure. Particular pains were taken to get higher accuracy in measuring the intensity fluctuations in the diffuse vibrational structure in the borazole. Positions of maxima and minima could be estimated visually to 2 or 3A on these bands.

BORAZOLE

Preparation[8]

Borazole, $B_3N_3H_6$, was prepared by the reaction between diborane and ammonia using a modification of the procedure given by Schlesinger, Ritter, and Burg.[9] Ammonia, about 2 liters, is carefully condensed in a uniform film on the wall of a 1-liter reaction tube which is provided with a side-arm break-off tip and attached to a vacuum apparatus. Diborane, exactly one mole for each two moles of ammonia taken, is condensed on to the ammonia film by means of liquid nitrogen. The reaction tube is allowed to warm slowly to −112°C, and it is allowed to stand at this temperature until the total pressure is less than 0.5 mm. The tube is then evacuated for several minutes, sealed from the vacuum apparatus, and immediately placed in a furnace at 300°C for 30 minutes. The reaction tube is reattached to the vacuum apparatus by means of a tube-opener, cooled with liquid nitrogen, opened, and the hydrogen removed. The tube is heated to 60°C, and the volatile material is transferred to the vacuum apparatus for purification. The product is purified by fractional condensation through −80°C, −112°C, and −196°C baths. Pure borazole (vapor tension[1] at 0°C, 85.4 mm; observed, 85.3 mm) is trapped at −112°C. The yield is 35 to 40 percent based on the diborane taken.

The heptane solutions were prepared in the vacuum apparatus. The borazole was measured

as the gas (568 cc at 28°C and 138 mm pressure) and the *n*-heptane as the liquid (10.23 cc). The measured amounts of the two substances were distilled into a tube, sealed from the apparatus, and stored in the sealed tube until just before use.
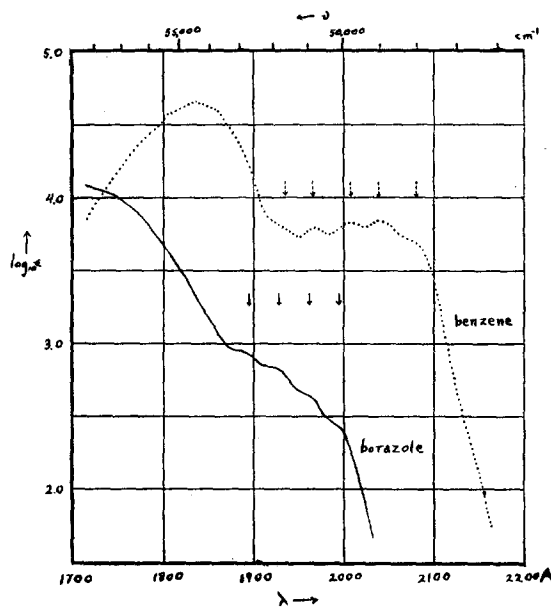

FIG. 1. Absorption spectrum of borazole ($B_3N_3H_6$) and benzene in *n*-heptane solution.

Spectrum

The absorption spectrum of the borazole in *n*-heptane solution is shown in Fig. 1, together with the spectrum of benzene in *n*-heptane solution for comparison. The benzene curve is taken from another paper.[10] The positions of the maxima in the 2000A region, as estimated visually, are indicated by arrows on the graph. In borazole, these maxima are as follows:

1995A	50,100 cm^{-1}
1962	50,950
1928	51,850
1895	52,750

The spacing in this series is about 900 cm^{-1}. Within the accuracy of measurement this may be taken to agree with either of the totally symmetric frequencies, 851 and 938 cm^{-1}, already

[8] The experimental methods used in the chemical part of this work are described in the publications of Schlesinger and co-workers, Chem. Rev. **31**, 1 (1942) and of Stock, *The Hydrides of Silicon and Boron* (Cornell University Press, Ithaca, New York, 1933).

[9] H. I. Schlesinger, D. M. Ritter, and A. B. Burg, J. Am. Chem. Soc. **60**, 1296 (1938).

[10] J. R. Platt and H. B. Klevens, Paper presented at Symposium on Color and Electronic Spectra of Complex Molecules, Division of Physical and Inorganic Chemistry of the American Chemical Society meeting at Evanston, Illinois, December 30–31, 1946 (to be published in Chem. Rev.).

known in the ground state.[5] In benzene, also, the excited states show little change in the breathing frequency.

At shorter wave-lengths, the absorption curve of borazole rises to intensities characteristic only
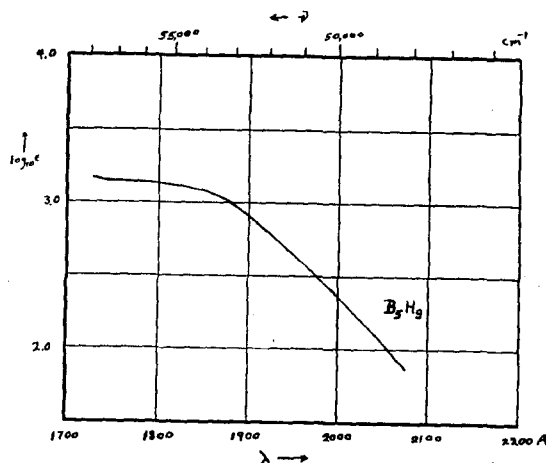

FIG. 2. Spectrum of B_5H_9 in n-heptane solution.

of $N \rightarrow V$ transitions.[11] The peak must lie below 1720A.

DISCUSSION

If we assume complete sharing of the free electron pair on each nitrogen by a boron and nitrogen atom together, the electronic structure of borazole becomes identical with that of benzene. One would expect, therefore, the upper levels of the borazole to correspond with those of benzene and the same characteristic bands to be present in both spectra.[12]

·[11] The notation $N \rightarrow V$ for certain transitions in olefins and ring compounds is attributable to Mulliken. See Mulliken and Rieke, Rep. Prog. Phys. (Phys. Soc. Lond., 1941) 8, 231.

[12] Professor R. S. Mulliken has shown that a detailed theoretical analysis supports this conclusion. We are indebted to him for the following statement which he has prepared for inclusion here:

"In benzene, the absorption regions $\lambda 2600$, $\lambda 2000$, and $\lambda 1800$ are believed to correspond to transitions from a $^1A_{1g}$ normal state having electron configuration $\cdots (1a_{2u})^2 (1e_{1g})^4$, to the three respective states $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$ of the excited electron configuration $\cdots (1a_{2u})^2 (1e_{1g})^3 1e_{2u}$. The symbols are group theory symbols of the usual type for over-all electronic states (capital letters) or for outer-electron molecular orbitals (small letters), and appropriate to the symmetry group of benzene (D_{6h}). The transitions $^1A_{1g} \rightarrow {}^1B_{2u}$ and $^1A_{1g} \rightarrow {}^1B_{1u}$ are forbidden according to the electronic selection rules for symmetry D_{6h}, while $^1A_{1g} \rightarrow {}^1E_{1u}$ is strongly allowed for radiation with electric vector vibrating in the plane of the molecule.

"The symmetry of borazole, assuming a planar arrangement of maximum symmetry, is D_{3h}. Although this sym-

The striking similarity of the spectra is seen in Fig. 1. It appears that the diffuse series in borazole starting at 1995A may be identified with the diffuse benzene $^1A_{1g} \rightarrow {}^1B_{1u}$ series starting at 2080A.[13] The strong continuum in borazole rising to a peak at 1720A or below must then correspond to the $^1A_{1g} \rightarrow {}^1E_{1u}$ benzene peak at 1830A (also called the $N \rightarrow V$ transition).

Against these identifications is the low intensity of the 1995 borazole bands and the failure to find bands like the 2600A benzene group, even though the highest borazole concentration used was twenty times as strong as that necessary for detecting these bands in benzene.

Nevertheless, three aspects of the spectrum favor this assignment. First, there is the smallness of the frequency shifts between the borazole and benzene spectra if we adopt this assignment —only 2000 cm⁻¹ shift for the 1995A group, and perhaps 4000 or 5000 cm⁻¹ for the $N \rightarrow V$ peak; any other correspondence between the bands would involve much larger wave-length shifts. Second, there is the similarity in appearance between the 1995A and 2080A groups. The diffuse 1995A group is only slightly more diffuse than the 2080A group and does not look anything like the sharp, strongly shaded bands of the 2600A benzene group, nor like the almost structureless $N \rightarrow V$ peak. Third, there is the very great absorption intensity of borazole at 1720A, with a molar extinction, ϵ, of over 10,000/mole-cm, which is stronger than has been

metry is lower than that of benzene, nevertheless it can be shown that a one-to-one correspondence and a close resemblance between the electron configurations and over-all states of borazole and benzene are to be expected. Using symbols appropriate to D_{3h} symmetry, the normal state should be a $^1A_1'$ state of configuration $\cdots (1a_2'')^2 (1e'')^4$, and there should be low excited states $^1A_2'$, $^1A_1'$, and $^1E'$, all of electron configuration $\cdots (1a_2'')^2 (1e'')^3 2e''$. (Here, as in benzene, there should also, of course, be corresponding triplet states.) Further, the transitions from the $^1A_1'$ to the $^1A_2'$ and $^1A_1'$ excited states are forbidden by the electronic selection rules, while that to the $^1E'$ state is strongly allowed for radiation with dipole moment vibrating in the molecular plane, in complete analogy to benzene.

"The analogy extends even further. In benzene, the occurrence of the 'forbidden' transitions $^1A_{1g} \rightarrow {}^1B_{2u}$ and $^1A_{1g} \rightarrow {}^1B_{1u}$ is explained mainly by coupling (of the upper or lower) electronic state with a degenerate vibration of class E_{2g} (the same for both transitions). In close analogy, the occurrence of $^1A_1' \rightarrow {}^1A_2'$ and $^1A_1' \rightarrow {}^1A_1'$ in borazole would be expected through coupling with a degenerate vibration of class E' (the same for both transitions)."

[13] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).

observed in this region in solution for any but $N \rightarrow V$ transitions.

These similarities then lend further support to the postulated ring structure and electronic structure of borazole.

But then the problem arises of explaining the relative weakness of the 1995A group in borazole and the absence of any group near 2600A. However, since in benzene these are forbidden transitions deriving their strength from interaction with the allowed $N \rightarrow V$ transition through electronic-vibrational coupling,[12, 13] it may be that the interaction constant for the 1995A transition is simply smaller in borazole by a factor of 10 or more. Perhaps this constant is relatively smaller still for the bands corresponding to the 2600A group, and as a result they have not been found simply because high enough concentrations or vapor pressures have not yet been used.

The relation between benzene and borazole is like that between graphite and boron nitride crystals. It is well known that the BN is built up of hexagonal "borazole" units (with hydrogens omitted) as graphite is built of "benzene" units.

The physical characteristics of graphite, with its infinite lattice of conjugated double bonds, are closely duplicated in boron nitride. The only great change is one of color—from black to white. This may be related to the changes found here in going from benzene to borazole—a shift of the spectrum to shorter wave-lengths and a great relative weakening of the long wave-length bands. The electrical characteristics of BN, such as its semiconductivity and photo-conductivity in the ultraviolet, deserve to be investigated for the light they may throw on these relationships.

A BORON HYDRIDE

We have also obtained the spectrum of one of the boron hydrides, B_5H_9, in n-heptane solution in the same wave-length region. Dr. A. E. Finholt kindly made up the sample for us in the solution. The observed spectrum is shown in Fig. 2. It is a featureless continuum, increasing in intensity to a molar extinction of over 1500 per mole-cm below 1740A. There is too little structure to make possible any conclusions for or against current theories of the B_5H_9 molecule.[14] Vapor measurements at shorter wave-lengths are indicated to be necessary.

We wish to thank our colleagues in the Physics and Chemistry Departments, and in particular Professor R. S. Mulliken, for helpful discussions on the interpretation of these spectra.

---

[14] K. S. Pitzer, J. Am. Chem. Soc. 67, 1126 (1945).