atom of nickel would produce a structure in which four out of six nickel atoms would be octahedral (thus paramagnetic) and the remainder planar (diamagnetic). The calculated theoretical moment for the hydrated sample (*i.e.*) $Ni(CN)_2(NH_3 \cdot {}^1/_3H_2O \times C_6H_6)$ is 2.2 B.M. and for the anhydrous sample, 1.9 B.M.[20]

The accuracy of our measurements does not permit us to make a decision concerning the coördination of water. The precision of our measurements would enable us to decide if we could examine an anhydrous sample. This was not possible, for attempts to dehydrate the hydrated material resulted in a loss of ammonia as well as water. This observation indicates the water may be coördinated.

Though the magnetic data do not distinguish between coördinated and free water, it is conclusively established that contrary to the information presently in the literature[3,4] these clathrates contain diamagnetic nickel atoms. The structure is represented as a hybrid of those presented in Fig. 1. Structure B has no effect upon the magnetic properties and is proposed to explain the short nickel to carbon distance found by the X-ray studies.[4] The bond arises from the overlap of a filled "d-orbital" of the nickel atom and an empty "p-orbital" of the carbon atom. Many structures similar to B representing different numbers of cyanide groups participating in this $d\pi$–$p\pi$ interaction are possible. The water has not been indicated in this figure, but if it is coördinated, there are probably two molecules on one out of every three or four planar nickel atoms.

Added in proof.—These results indicate that conclusions regarding the coördination of ligands to metal ions, based upon changes of the infrared spectra of solid materials are not reliable. In this work, shifts of the order of magnitude of 50 cm.$^{-1}$ were observed when the organic molecule was placed in the crystal lattice of the clathrate. Similarly, many of the spectral changes observed upon coördination of a ligand to a metal ion could be caused by similar interactions.

Acknowledgments.—The authors wishes to acknowledge with thanks the Karl Fischer determination of water carried out by Mr. F. M. Wachi. Thanks also are due to Mr. James Brader for measuring the infrared spectra on the many samples of clathrates which were prepared.

Urbana, Illinois

[20] The approximate theoretical magnetic moment (μ mean) was calculated by taking the root mean square of the magnetic moments of the various nickel atoms. For example, consider the compound $Ni(CN)_2NH_3{}^1/_3H_2O$, μ mean = $[(3\mu_1^2 + 2\mu_2^2 + 1\mu_3^2)/6]^{1/2}$ where μ_1 is the moment for each of the three nickel atoms with two ammonias (2.73 B.M.), μ_3 for the one with two waters (2.73 B.M.) and μ_2 for each of the two planar diamagnetic nickel atoms (0.0 B.M.).

[Contribution from the Department of Chemistry, Iowa State College, and Varian Associates]

Structures of Halogen Substituted Boranes

By Riley Schaeffer,[1] James N. Shoolery[2] and Robert Jones

Received December 11, 1957

The nuclear magnetic resonance spectra of several halogen substituted boranes have been observed and used to establish conclusively the structures. Both a monoiodide and a monobromide of pentaborane-9 have been shown to be apex substituted. A monoiodide and a monobromide of decaborane have been shown to be substituted at the B-2 positions. A second monoiodide of decaborane could not be conclusively assigned a structure but is most probably substituted at the B-1 position.

Relatively few substitution products of the higher boranes have been described and the structure of only one of them ($B_{10}H_{12}I_2$) has been established.[3] The method of preparation of $B_{10}H_{12}I_2$ and its structure both suggest that it is formed by electrophilic attack of the I^+ species at a region of high electron density in the electron deficient decaborane molecule.[4] Other boranes, particularly the two pentaboranes, would be expected to undergo similar reactions to form products with structures in accord with the above mechanism. Thus, both pentaboranes should form monohalides by substitution in the apex position. Since five new monohalides of the boranes were available to us, we desired a method of structural determination which would not only be completely reliable but would also be relatively rapid. Nuclear magnetic resonance spectroscopy seemed to be ideally suited for such work.

Experimental

The five new substituted boranes available to us were: B_5H_8Br (m.p. 32–34°), B_5H_8I (m.p. 53°), $B_{10}H_{13}Br$ (m.p. 105°), $B_{10}H_{13}I$ (m.p. 116°) and $B_{10}H_{13}I$ (m.p. 72°). Approximately 20% solutions of each of the compounds in pure, dry carbon disulfide were prepared in 6 mm. Pyrex tubes and sealed. A solution of $B_{10}H_{12}I_2$ also was prepared using material previously studied by X-ray diffraction techniques.[3] The tubes were stored at −80° whenever they were not being used for spectral observations.

Both proton and B^{11} nuclear magnetic resonance spectra were obtained using a Varian Associates model No. V-4300 B high resolution spectrometer. Proton spectra were obtained both in the usual manner at 30 Mc./sec. and also using a double tuned circuit resonant at both 30.0013 and 9.6257 Mc./sec. The effect of the latter method is to interrupt the spin orientations of the B^{11} nuclei frequently enough so that the H^1 nuclei see only the average value of zero and the multiplet structure collapses.[5] All spectra are shown with field strength increasing toward the right.

Results

Figure 1 compares the proton resonance spectrum of B_5H_8Br and B_5H_8I with that of B_5H_9. The

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[2] Varian Associates, Palo Alto, California.

[3] R. Schaeffer, This Journal, **79**, 2726 (1957).

[4] For the suggestion that electrophilic substitution may occur in boranes see W. N. Lipscomb, *J. chim. phys.*, **53**, 515 (1956). For a discussion of charge distribution in boranes see W. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

[5] (a) A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, **97**, 1261 (1955); (b) J. N. Shoolery, *Disc. Faraday Soc.*, **19**, 215 (1955).

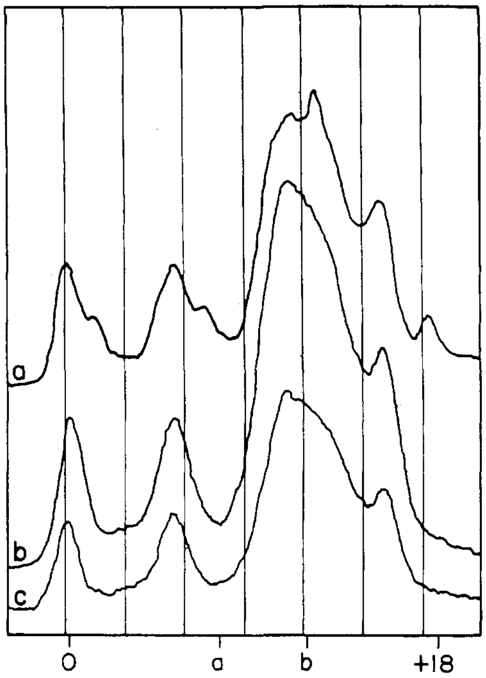

Fig. 1.—^{1}H magnetic resonance spectra of: (a) B_5H_9; (b) B_5H_8Br; (c) B_5H_8I.

complete disappearance in the substituted boranes of the weaker quartet which appears superimposed on the high field tail of the larger quartet in the pentaborane spectrum[6] clearly shows that the haloboranes are apex substituted. The elimination of the component of the quartet at +18 p.p.m. is most apparent.

Figure 2 shows the proton spectrum of the substituted compounds using the double tuned circuit. Although in pentaborane-9 two saturating frequencies (presumably separated by the basal–apex borane chemical shift) could be found which would produce peaks in the proton spectra associated with the corresponding protons, only one saturating frequency produced peaking in the proton spectra of the halo pentaboranes. Furthermore, the two peaks observed are of equal intensity and show that equal numbers of bridge and basal protons still remain.

The conclusion reached above on the basis of the proton spectra is fully confirmed by the B^{11} spectra shown in Fig. 3. It can be seen that the halogen substituted boranes still retain the large doublet arising from the basal borons but the small apex related doublet has in each spectrum collapsed to a single peak of doubled intensity. This collapse of the doublet occurs in spite of the spins of the bromine and iodine nuclei because nuclei with large electric quadrupole moments undergo many changes of spin state during a time which is quite short compared to the reciprocal of the spin–spin coupling constant of the boron nucleus bonded to them.

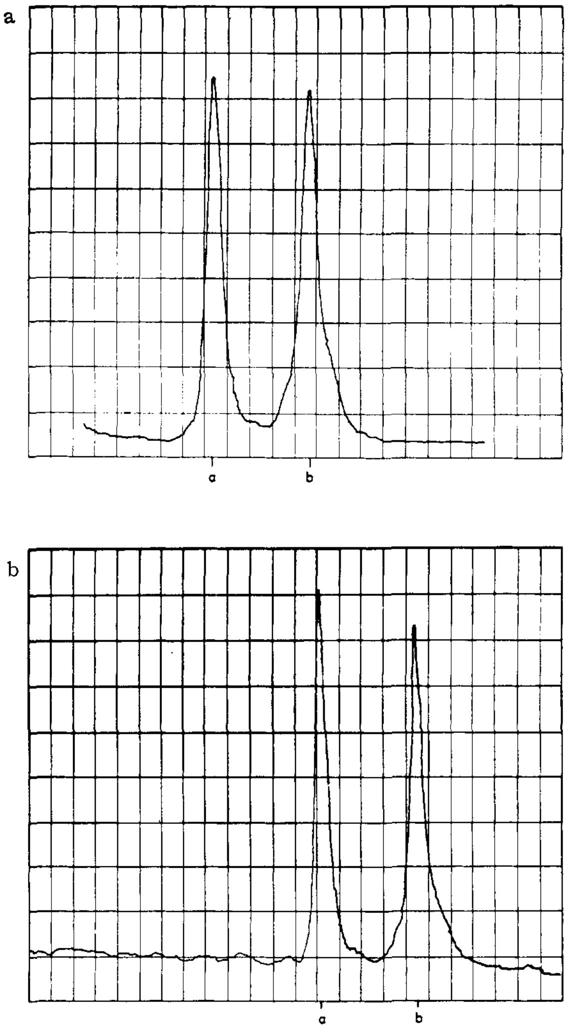

Fig. 2.—H′ magnetic resonance spectrum of: B_5H_8Br (a) with B″ excited at 9.6257 Mc./sec.; B_5H_8I (b) with B″ excited at 9.6257 Mc./sec.

Neither the proton nor the B^{11} spectrum of decaborane contains sufficient lines to permit a simple identification of one absorption peak with each type of structurally different atom. However, the B^{11} spectrum does contain one well isolated doublet arising from a peak owing to two structurally equivalent boron atoms split by coupling of each boron to a single hydrogen with a spin of $^1/_2$. Assignment of this doublet to the two B-2 boron atoms is conclusively confirmed by the B^{11} spectrum of $B_{10}H_{12}I_2$ shown in Fig. 4b.[7] Collapse of the doublet to a single peak in the same fashion as in the pentaborane spectra discussed above shows that the borons bonded in this molecule to iodine are responsible for the high field doublet in the unsubstituted mole-

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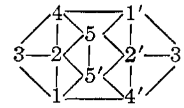
(6) For a discussion of the spectra of boranes see footnote 5b and R. Schaeffer, J. N. Shoolery and R. Jones, THIS JOURNAL, **79**, 4606 (1957).

(7) The numbering system used here is that of J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950). For convenience, it is reproduced here in the form of the usual projection down the twofold axis. This numbering is retained in spite of the current preference of



the nomenclature committee since structurally equivalent borons are given unrelated numbers on the basis of their recommended ring index. Of course, the 1,4-borons are also equivalent in the above system but it seems best to adopt *in toto* the previously used system unless a ring index is proposed which retains structural significance.

Fig. 3.—^{11}B magnetic resonance spectra of: (a) B_5H_9; (b) B_5H_8Br; (c) B_5H_8I.

cule. The iodine atoms in $B_{10}H_{12}I_2$ have previously been shown by single crystal X-ray diffraction studies to be at the B-2 positions.[3]

The single isomer of monobromodecaborane and the higher melting (116°) monoiododecaborane are also substituted in the B-2 position as shown by the spectra in Figs. 4c and d. In both cases only partial collapse of the doublet occurs, of course, since one hydrogen remains on a B-2 boron to produce a doublet of one half the original intensity. It is interesting to observe the shift of the peak to higher fields which occurs in the series from the monobromo to the parent hydride to the monoiodide in a manner which qualitatively could be ascribed to an increasing electron density around the B-2 boron atom as a result of unbalance of p-electrons along the bond direction similar to that observed for fluorine compounds.[8,9] The series is not long enough nor the connection between electron density and position of absorption peak simple enough to justify this conclusion in an absolute manner.

In an equally clear fashion, Fig. 4e shows that the lower melting (72°) iodide is not substituted in the B-2 position. An attempt to establish its structure from the nuclear magnetic resonance spectrum alone leads one into the realm of probabilities if not mere possibilities. However, if one can assume that, as with the other monoiodide, the collapsed peak will fall somewhat to the right or higher field side of the center of gravity of the original peak, then substitution has affected the doublet (one of two giving the apparent triplet structure at the low field side of the spectrum)[6] at the higher field side of the apparent triplet. If the tentative assignment of this doublet to accidental overlap of the B-3 and B-5 absorptions is correct,[6,10] the lower melting iodide then would be substituted at one of these two positions. No more certain conclusion can be drawn at this stage but determination of the structure of this iodide by independent means would also confirm the tentative spectral assignment.

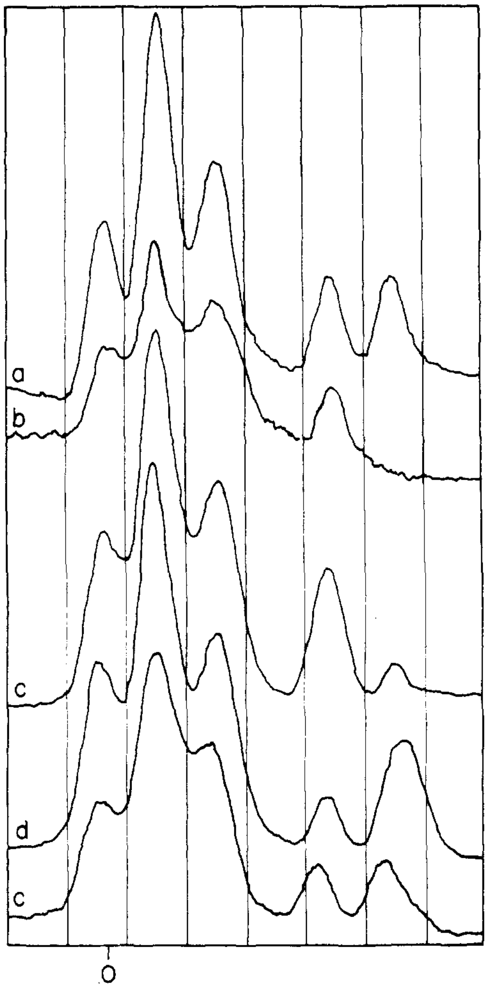


Fig. 4.—^{11}B magnetic resonance spectra of: (a) $B_{10}H_{14}$; (b) $B_{10}H_{12}I_2$; (c) $B_{10}H_{13}Br$; (d) $B_{10}H_{13}I$ (m.p. 116°); (e) $B_{10}H_{13}I$ (m.p. 72°).

Discussion

The structures which have been conclusively established in this work are in agreement with the predictions made in earlier work concerning the electrophilic nature of the halogenation reaction. The formation of a second isomer of monoiododecaborane is not necessarily in conflict with this interpretation but could result from a competing reaction at a site of somewhat lower electron density. It is also easily possible that both polar and radical attack occurs leading to different isomers. It serves to warn, however, against undue reliance in or

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(8) It was first pointed out by Professor William Lipscomb that the order is that of increasing polarizability of the substituted atom.

(9) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(10) Recent studies give strong evidence that the original assignment is inverted with the fourfold set of borons giving rise to the higher field component of the apparent triplet. A forthcoming paper in This Journal will present this evidence. It appears quite probable on the basis of the reassignment that the lower melting iodide is substituted on the B-1 atom.

extension of the postulated mechanism in the absence of further experimental confirmation.

Acknowledgment.—This work was made possible in large part by a grant to one of us (R.S.) from the Iowa State College Alumni Achievement Fund to cover travel expenses incurred during the investigation, and this assistance is gratefully acknowledged.

[CONTRIBUTION FROM THE RADIOMETRY SECTION, ATOMIC AND RADIATION PHYSICS DIVISION, NATIONAL BUREAU OF STANDARDS]

The Structure of Ethylene from Infrared Spectra[1]

BY HARRY C. ALLEN, JR., AND EARLE K. PLYLER

RECEIVED JANUARY 13, 1958

From an analysis of the parallel band of C_2H_4 at 2988.66 cm.$^{-1}$ and the parallel band of C_2D_4 at 2201.013 cm.$^{-1}$ the inertial constants B and C for each molecule in the ground vibrational state were determined as $B = 0.9998$, $C = 0.8294$ and $B = 0.7334$, $C = 0.5636$, respectively. From these inertial constants the molecular parameters are deduced to be $r_{CC} = 1.337$ Å., $r_{CH} = 1.086$ Å. and $<_{\mathrm{HCH}} = 177°22'$.

Introduction

Ethylene is one of the few relatively simple molecules for which there are still no adequate structural data. This molecule is very nearly a symmetric rotor, *i.e.*, the two large moments of inertia are nearly equal, and as a result previous studies[2,3] of the infrared spectrum have all been interpreted on a symmetric rotor model. The rotational Raman effect also has been observed,[4] but again the analysis was on the basis of a pseudo-symmetric rotor model.

In this type of analysis it is not possible to determine B and C directly but only $^1/_2\ (B + C)$. In order to make the separation of B and C, it is necessary to invoke the condition that $I_C = I_A + I_B$ which only holds for rigid planar bodies. This condition can introduce sizable errors into the structural parameters.

With the spectrometers available in this Laboratory it is possible to resolve the rotational fine structure due to the inequality of I_B and I_C and thus determine these parameters directly from the analysis of the data. This allows the determination of the structural parameters without assuming any relationship among the moments of inertia.

Experimental

The spectra were recorded with the grating instruments of the Radiometry Section[5] using a 10,000 line/in. grating with a ruled surface of about 6 by 8 inches. For the wave lengths shorter than 3.5 μ a cooled PbS cell was used as a detector while at longer wave lengths a cooled PbTe cell was used.

The band in both molecules was quite intense so could be observed at very low pressures. The C_2H_4 band was observed with pressures as low as 0.3 mm. of gas in a 1 m. cell while pressures as low as 1 mm. of C_2D_4 were used in the same cell. The wave lengths of the lines were measured by employing a Fabry–Perot interferometer as previously described.[6]

In the C_2H_4 band at 2988 cm.$^{-1}$, lines separated by 0.04 cm.$^{-1}$ were clearly resolved while in the C_2D_4 band at 2200 cm.$^{-1}$ the resolution was somewhat poorer, about 0.08 cm.$^{-1}$. Figures 1 and 2 are reproductions of recorder traces of the two bands made on white chart paper.

Analysis, C_2H_4

The C_2H_4 band near 2988 cm.$^{-1}$ is a parallel type band, *i.e.*, electric moment changes along the least inertial axis. The selection rules in the symmetric limit are $\Delta J = 0, \pm 1, \Delta K = 0$. In this limit the rotational levels for $K \neq 0$ are all doubly degenerate. If the inertial constants in the two vibrational states are nearly equal, then for each $\Delta J = \pm 1$ one would expect all the transitions for the various K to fall on top of each other giving rise to a series of equally spaced lines in the P and R branches. However, if $I_B \approx I_C$, the first-order perturbation causes a splitting of the $K = 1$ levels in each vibrational state. The selection rules for J remain the same, and likewise for K except that parity of asymmetric rotor wave functions must be considered leading to the selection rules[8] ee $\longleftrightarrow$ eo, oo $\longleftrightarrow$ oe. As a result for a given $\Delta J = \pm 1$, all the K transitions except those with $K = 1$ will fall on top of each other, and the two transitions with $K = 1$ will fall one on each side of the main grouping. Hence in this approximation, each P and R branch transition for a given J will appear as a triplet. As the quantity $B - C$ becomes large, higher order corrections to the energy enter and the splitting becomes more complex especially as J becomes higher. The simple triplet structure is clearly evident for P_2, P_3, R_1, R_2, R_3 in Fig. 1 although the splitting quickly becomes more complicated as J increases.

A set of C_2H_4 energy levels was calculated using Lord's[3] values for the inertial constants and published energy tables.[7]

From these energy values a trial spectrum was calculated using A-type selection rules,[8] (ee $\longleftrightarrow$ oe, oo $\longleftrightarrow$ eo) and relative intensities obtained by combining the line strengths[9] for $\kappa = -0.9$ with the appropriate Boltzmann and nuclear spin factors. For a planar model of C_2H_4 the nuclear

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(1) The work reported herein was supported by the U. S. Atomic Energy Commission.

(2) W. S. Gallaway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942).

(3) R. C. Lord, Final Technical Report, "Techniques of Infrared Spectroscopy," Spectroscopy Laboratory, Massachusetts Institute of Technology, December, 1955.

(4) Romanko, Feldman, Stansbury and McKellar, *Can. J. Phys.*, **32**, 735 (1954).

(5) N. Gailar and E. K. Plyler, *J. Research Natl. Bur. Standards*, **45**, 102 (1955).

(6) E. K. Plyler, L. R. Blaine and E. D. Tidwell, *ibid.*, **55**, 279 (1955).

(7) G. W. King, R. M. Hainer and P. C. Cross, *J. Chem. Phys.*, **11**, 27 (1943).

(8) P. C. Cross, R. M. Hainer and G. W. King, *ibid.*, **12**, 210 (1944).

(9) R. H. Schwendeman and V. W. Laurie, private communications.