state 430 kev above the ground state in the residual Be^7 nucleus which can be excited in $Li^7(p,n)Be^7$ reaction over the energy range covered in this experiment. The measurements made at Wisconsin[11] and preliminary measurements made in this laboratory show that about 10 percent of the Be^7 nuclei are left in the excited state. This makes it possible that some of the observed resonances could be due to the slower group of neutrons producing the same resonance that had been measured previously at some lower energy with the primary group of neutrons. However, when one considers that the second group makes up 10 percent of the total number of neutrons and that the cross section at most resonance energies increases by a factor of two over the average cross section, one finds that the second group can produce a resonance in the cross section which increases by only 7 percent above the average cross-section value. All measured resonances were considerably higher than this. Measurements which included this second group of neutrons were also improbable because the detector was energy-sensitive and was biased to discriminate against the smaller pulses produced by the slower neutrons. Since the detector was completely insensitive to neutrons with less than 550 kev, the measurements could not include any of the slower group until primary neutron energies of greater than 1 Mev were used. As the neutron energy was increased the bias on the pulse selector of the detector was increased to keep the counting rate approximately constant. By discriminating against smaller pulses in this way, it is felt that no neutrons of the slower group were detected at any time.

The measurements give total cross sections only. No attempt was made to find what part of the total cross section was due to scattering and what part arose from nuclear reactions.

An analysis of this data has not yet been completed, but it appears that there is no obvious similarity in the energy levels of the different compound nuclei which are formed when light nuclei containing an integral number of alpha-particles are bombarded by fast neutrons.

This work was materially assisted by the University of Minnesota Technical Research Fund subscribed to by General Mills, Inc., Minneapolis Honeywell Regulator Company, Minneapolis Star Journal and Tribune Company, Minnesota Mining and Manufacturing Company, and Northern States Power Company.

---

[10] T. Lauritsen and R. G. Thomas, Bull. Am. Phys. Soc. **24**, No. 8, 11 (1949).

[11] Johnson, Laubenstein, and Richards, Phys. Rev. **77**, 413 (1950).

PHYSICAL REVIEW VOLUME 78, NUMBER 5 JUNE 1, 1950

Microwave Determination of the Structure of Borine Carbonyl and of the Nuclear Moments of the Stable Boron Isotopes

Walter Gordy and Harold Ring*
Department of Physics, Duke University,† Durham, North Carolina
AND
Anton B. Burg
Department of Chemistry, University of Southern California,‡ Los Angeles, California

(Received February 2, 1950)

From measurements on the $J=1\rightarrow2$ and the $J=2\rightarrow3$ rotational transitions of borine carbonyl its molecular structure has been determined as follows: $d_{BH}=1.194A$, $d_{BC}=1.540A$, $d_{CO}=1.131A$, and $\angle HBH=113°52'$. The moments of inertia (which assume $h=6.624_2\times10^{-27}$ erg. sec.) in g $cm^2\times10^{-40}$ are: 93.42_{66} for $B^{10}H_3C^{12}O$, 96.90_{92} for $B^{11}H_3C^{12}O$, 111.41_{13} for $B^{10}D_3C^{12}O$, and 114.35_{40} for $B^{11}D_3C^{12}O$. Nuclear quadrupole couplings determined are 3.36 ± 0.10 mc/sec. for B^{10} and 1.55 ± 0.08 mc/sec. for B^{11}. Approximate values of the nuclear quadrupole moments are 0.06×10^{-24} cm^2 for B^{10} and 0.03×10^{-24} cm^2 for B^{11}. The nuclear spin of B^{10} is determined as 3 and that of B^{11} as 3/2.

1. INTRODUCTION

In preliminary communications[1] we have reported the experimental determination of the nuclear spins, quadrupole couplings, and approximate values for the quadrupole moments of B^{10} and B^{11}. Since our original report the spin values have been confirmed by remeasurement of the hyperfine structure with a new chemical sample of BH_3CO and by measurements on BD_3CO. Precision measurements have now been made on samples of both normal and deuterated borine carbonyl, and a complete determination of the structure of borine carbonyl has been made.

2. EXPERIMENTAL METHODS

For detecting the lines a single 1*N*26 crystal detector followed by a narrow-band, low frequency amplifier

---

* Frederick Gardner Cottrell Fellow. Now with the E. I. du Pont de Nemours Company, Wilmington, Delaware.

† The research at this University was supported by a grant-in-aid from the Research Corporation. It was submitted by H. Ring in partial fulfillment of the requirements for the Ph.D. degree.

‡ The work at this University was supported through a contract with the ONR.

[1] Gordy, Ring, and Burg, Phys. Rev. **74**, 1191 (1948); **75**, 1325(A) (1949).

TABLE I. Hyperfine spectrum of the $J=1\rightarrow 2$ transition.

		Frequency in mc/sec.		Relative intensity	
K	$F\rightarrow F'$	Calculated[a]	Observed	Calculated	Observed
		$B^{10}H_3C^{12}O$			
0	2→3	35,920.38	35,920.40	18	20
0	4→4	35,920.24	35,920.22	31	35
0	4→3	35,920.14		6	
0	2→2	35,919.96	35,919.95	30	25
0	4→5	35,919.64	35,919.60	100	200
0	3→4	35,919.57		51	
0	2→1	35,919.54		27	
0	3→3	35,919.47		40	
0	3→2	35,919.07	35,919.08	15	20
1	3→4	35,918.59	35,918.55	38	55
1	3→3	35,918.55		30	
1	3→2	35,918.35	35,918.29	11	25
1	4→4	35,918.26		23	
1	4→3	35,918.22		4	
1	2→3	35,918.11	—	13	—
1	4→5	35,917.96	35,917.96	75	80
1	2→2	35,917.90		23	
1	2→1	35,917.67	35,917.66	21	20
		$B^{11}H_3C^{12}O$			
0	1/2→3/2	34,629.27	34,629.27	21	40
0	5/2→5/2	34,629.23		23	
0	5/2→3/2	34,628.96	34,628.85	3	170
0	1/2→1/2	34,628.88		21	
0	3/2→5/2	34,628.85		53	
0	5/2→7/2	34,628.85		100	
0	3/2→3/2	34,628.57	34,628.58	27	30
0	3/2→1/2	34,628.18	34,628.16	4	5
1	3/2→5/2	34,627.81	34,627.81	39	35
1	3/2→3/2	34,627.68	34,627.64	20	25
1	5/2→5/2	34,627.62		17	
1	3/2→1/2	34,627.48	34,627.42	3	75
1	5/2→3/2	34,627.48		2	
1	5/2→7/2	34,627.43		75	
1	1/2→3/2	34,627.33		16	
1	1/2→1/2	34,627.13	34,627.16	16	20

TABLE I.—(*Continued*)

		Frequency in mc/sec.		Relative intensity	
K	$F\rightarrow F'$	Calculated[a]	Observed	Calculated	Observed
		$B^{10}D_3C^{12}O$			
0	2→3	30,122.00	30,121.86	18	40
0	4→4	30,121.86		31	
0	4→3	30,121.76		6	
0	2→2	30,121.58	30,121.56	30	25
0	4→5	30,121.26	30,121.21	100	200
0	3→4	30,121.19		51	
0	2→1	30,121.16		27	
0	3→3	30,121.09		40	
1	3→4	30,120.84	30,120.86	46	60
1	3→3	30,120.80		37	
0	3→2	30,120.69		15	
1	3→2	30,120.60	30,120.56	13	30
1	4→4	30,120.51		28	
1	4→3	30,120.47		5	
1	2→3	30,120.36	—	16	—
1	4→5	30,120.21	30,120.21	92	110
1	2→2	30,120.15		28	
1	2→1	30,119.92	30,119.91	26	30
		$B^{11}D_3C^{12}O$			
0	1/2→3/2	29,346.65	29,346.65	21	40
0	5/2→5/2	29,346.61		23	
0	5/2→3/2	29,346.34	29,346.24	3	170
0	1/2→1/2	29,346.26		21	
0	3/2→5/2	29,346.23		53	
0	5/2→7/2	29,346.23		100	
0	3/2→3/2	29,345.95	29,345.93	27	30
0	3/2→1/2	29,345.56	—	4	—
1	3/2→5/2	29,345.66	29,345.68	48	40
1	3/2→3/2	29,345.53	29,345.52	24	30
1	5/2→5/2	29,345.47		21	
1	3/2→1/2	29,345.33	29,345.28	4	100
1	5/2→3/2	29,345.33		2	
1	5/2→7/2	29,345.28		92	
1	1/2→3/2	29,345.18		20	
1	1/2→1/2	29,345.00	29,345.03	20	25

[a] Calculated with $I=3$ and 3/2, with $eQ(\partial^2V)/(\partial z^2)=3.36$ and 1.55 mc/sec. for B^{10} and B^{11}, respectively. In addition to the separation caused by quadrupole effects, the $K=1$ lines are separated from the $K=0$ lines by the centrifugal stretching term, $-4D_{J,K}$. The values used for $D_{J,K}$ are given in Table III.

was employed. Filtering[2] was used to eliminate the mode contour and effects of variations in power caused by impedance mismatch. The more sensitive modulation methods[3] could not be used on the $J=1\rightarrow 2$ transition because their distortion of the lines prevented resolution of the hyperfine structure. The absorption cell, which was 60 ft. in length, was made of coin silver K-band wave guide. Raytheon millimeter wave klystrons provided the microwave power.

Measurements of the line positions were made with frequency markers produced by multiplying to the microwave region a 10-mc/sec. signal continuously monitored by station WWV. Details of the standard[4] and the monitoring method[3] are given elsewhere.

3. NUCLEAR MOMENTS

Spins

Previous to our initial report, no determination of the spins of B^{10} and B^{11} had been made, although concurrently with that report there appeared the interesting note of Goldhaber[5] in which he, independently of our work, predicted from theoretical considerations the surprising value of 3 for the spin of B^{10}. Before that time the spin of B^{10} had been generally assumed to be 1, and that of B^{11} to be 3/2. Our observation confirms the spin of 3/2 for B^{11}, but proves that the spin of B^{10} is 3, in agreement with Goldhaber's prediction.

From the point of view of simplicity of spectrum, as well as of chemical and physical behavior, borine carbonyl appeared to be the most satisfactory molecule from which to determine the spins of the boron isotopes by means of microwave spectroscopy. However, because these nuclei are small in size, a large quadrupole moment was not expected for either. And because the electron diffraction data[6] indicated a molecular structure which could be explained on the basis of tetrahedral bonds to the boron, we were not very hopeful at the outset that a resolution of the hyperfine structure

---

[2] W. Gordy and M. Kessler, Phys. Rev. **71**, 640 (1947).

[3] W. Gordy, Rev. Mod. Phys. **20**, 668 (1948).

[4] R. Unterberger and W. V. Smith, Rev. Sci. Inst. **19**, 580 (1948).

[5] M. Goldhaber, Phys. Rev. **74**, 1194 (1948).

[6] S. H. Bauer, J. Am. Chem. Soc. **59**, 1804 (1937).

would be possible. Fortunately, the HBH angles proved to be larger than tetrahedral and the quadrupole coupling just large enough to allow determination of the spins of both B^{10} and B^{11}. It is also fortunate that the centrifugal stretching in the BH_3CO molecule is so large that the hyperfine structure of the $K=0$ lines is completely separated from that of the $K=1$ lines. For BD_3CO this is not quite true. For this reason the spin determinations from the latter molecule are not quite as definite as those from BH_3CO, although they do provide confirming evidence. See Table I.

The transition by which we were able to establish the spins is $J=1\rightarrow2$, which for $B^{10}H_3CO$ occurs at 35919 mc/sec. The hyperfine structure of the $J=0\rightarrow1$ transition, which contains only three lines, is more widely spaced than that of the $J=1\rightarrow2$. Nevertheless, because its absorption is much weaker than that of the $J=1\rightarrow2$, we were unable to detect its lines at the extremely low pressures required for their resolution. The absorption at the $J=2\rightarrow3$ transition is of course, stronger than that at the $J=1\rightarrow2$. But in the $J=2\rightarrow3$ transition the hyperfine structure is so closely spaced that we were unable to resolve it, although we could detect a broadening of the $K=2$ and the $K=3$ lines caused by the quadrupole coupling. The sample contained B^{10} in normal concentration, about 18 percent. With our spectrometer one could obtain complete resolution of the $J=0\rightarrow1$ transition by using a sample containing a high concentration of the B^{10} isotope, also a better resolution of the $J=1\rightarrow2$ transition. Since the data obtained were considered adequate to establish the spin, we did not prepare a sample with concentrated B^{10}. By using the Stark modulation method[7] one can obtain higher sensitivity, but the consequent complication of the pattern decreases the resolution and might prevent identification of the spin. Indeed, Strandberg, Pearsall, and Weiss[8] have observed the $J=0\rightarrow1$ transition with the Stark modulation method but were unable to resolve the hyperfine structure.[9]

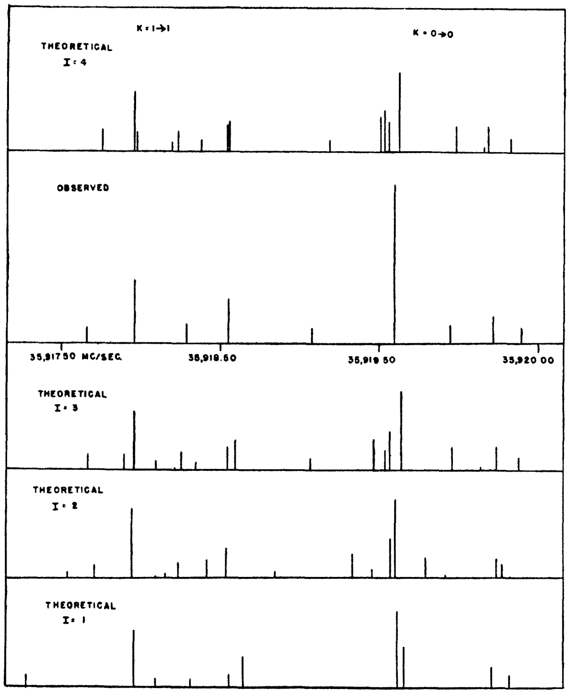


FIG. 1. Observed and calculated hyperfine structure of the $J=1\rightarrow2$ transition of $B^{10}H_3CO$.

Figure 1 shows the positions and estimated intensities of the observed lines, compared with the theoretically predicted patterns for different spin values which might be considered possible. It is apparent that the spin of 3 is the only one consistent with the observed data.[10] In Fig. 2 are shown two photographs of the C.R.O. presentation of the hyperfine structure. The measurements of the lines are more certain than the pictures indicate, since the adjustment of conditions for the over-all picture was not as favorable as was possible when adjustments were optimized for a certain portion. Also, the measurements were checked many times under different conditions of observation, and on $B^{10}D_3CO$ as well as $B^{10}H_3CO$. See Table I.

Figure 3 and Table I compare the calculated and observed hyperfine structure for the $J=1\rightarrow2$ transition of $B^{11}H_3CO$. These comparisons demonstrate that the nuclear spin of B^{11} is 3/2.

Quadrupole Moments

The nuclear quadrupole coupling $eQ(\partial^2V)/(\partial z^2)$ is calculated from the formula:

$$E_Q=eQ\frac{\partial^2V}{\partial z^2}\left(\frac{3K^2}{J(J+1)}-1\right)\times\left(\frac{\frac{3}{4}C(C+1)-I(I+1)J(J+1)}{2(2J+3)(2J-1)I(2I-1)}\right),$$

where $C=F(F+1)-I(I+1)-J(J+1)$, $F=J+I$, $J+I-1\cdots|J-I|$, $I=$spin of the interacting nucleus, and $J=$rotational quantum number. Table I gives the observed hyperfine structure for the $J=1\rightarrow2$ transition of $B^{10}H_3CO$, $B^{10}D_3CO$, $B^{11}H_3CO$, and $B^{11}D_3CO$ with that calculated from the above formula, using $eQ(\partial^2V)/(\partial z^2)=3.36$ mc/sec. for B^{10} and 1.55 mc/sec. for B^{11}. These we consider the most probable values for the respective couplings. They give the ratio of the quadrupole moment of B^{10} to that of B^{11} as 2.17 and show that both the moments are of the same sign.

---

[7] R. H. Hughes and E. B. Wilson, Phys. Rev. **71**, 562 (1947).

[8] Strandberg, Pearsall, and Weiss, J. Chem. Phys. **17**, 429 (1949).

[9] After this was written we learned by private communication that Weiss, Strandberg, Lawrance, and Loomis have now been able to check our spin assignment with the Stark modulation method.

[10] The calculated spectra for spin values of 2 and 4, which are closest to the correct value, have certain frequency ratios which differ from the corresponding observed ratios by a factor outside the range of experimental error.

To obtain the quadrupole moment Q from the measured quadrupole coupling, one must evaluate the quantity $(\partial^2 V)/(\partial z^2)$, which represents the gradient along the symmetry axis of the electric field of the extra nuclear electrons. An exact calculation of this quantity is not possible for borine carbonyl, but from the molecular structure determinations given below one can obtain an approximate value. As indicated below, the structure of borine carbonyl may be considered as a resonant hybrid of structures I to V. The value of $(\partial^2 V)/(\partial z^2)$ can be calculated approximately for these contributing structures. To obtain its value for the actual molecule we average the values for these structures in proportion to their estimated contributions to the ground state of the molecule.

In structures I and II, with four equivalent tetrahedral bonds to boron, the valence shell of B is symmetrically filled; and, except for second-order polarization effects, which we discuss below, $(\partial^2 V)/(\partial z^2)$ would be zero. This is also true, to a first approximation, for III and IV. In the most important case, structure V, where we have essentially free BH_3 and CO, there are, from analogy with BF_3, three equivalent sp^2 bonds to boron which lie in a plane at angles of 120°. The p orbital perpendicular to this plane and along the symmetry axis of the molecule contains no electrons. Following the practice of Townes,[11] we estimate $(\partial^2 V)/(\partial z^2)$ for this case from the formula,

$$(\partial^2 V)/(\partial z^2)=\frac{2\epsilon\Delta\nu l(l+1)}{Z_i R\alpha^2 a_0^3(2l-1)(l+\frac{1}{2})(2l+3)},$$

used to calculate the coupling of electrons in isolated atoms.[12] It is clear that there is an equivalent deficit of one p electron along the molecular axis and hence that $(\partial^2 V)/(\partial z^2)$ would be positive in sign. From the value of $\Delta\nu=15$ cm^{-1}, taken from Bacher and Goudsmit,[13] and with $Z_{\text{eff}}=3.1$, we obtain $(\partial^2 V)/(\partial z^2)=1.44\times 10^{15}$ e.s.u. for this case.

The contributions to $(\partial^2 V)/(\partial z^2)$ by the excited electronic states can be neglected in the present approximation. Also, the effects of bond-orbital overlap are negligible. Distortion of the bond orbitals by the adjacent atoms requires consideration. In structures I and II the distortion effects would be in the same direction along each bond and would tend to cancel each other. Though the carbon is further from the boron than are the hydrogens, its greater electronegativity and its positive formal charge in II would still allow it to counterbalance approximately the effects of the hydrogens. In III and IV the distortion effects would tend to cancel each other but to a lesser extent than in I and II since the bond angles would not be exactly tetrahedral. For these structures a small negative contribution to $(\partial^2 V)/(\partial z^2)$ might be expected. In structure V we neglect the effects of the CO group since here it is effectively free carbon monoxide, which is known to have a very small dipole moment (~0.1 debye). Fortunately, hydrogen and boron have almost the same electronegativities, 2.1 and 2.0, and consequently the ionic character of the BH bonds will be very small. The most apparent effects of the hydrogens would be to flatten slightly the boron atomic orbitals in the BH_3 plane and hence to increase $(\partial^2 V)/(\partial z^2)$. One can estimate the order of magnitude of the hydrogen effects by a comparison with the $(\partial^2 V)/(\partial z^2)$ for the hydrogen molecule, which is due almost entirely to distortion of the s orbitals. This quantity has been calculated for H_2 by Nordsieck[14] as 1.15×10^{15} e.s.u. Since the hydrogen-boron separation in BH_3 ($d_{BH}=1.194$A) is much greater than the hydrogen separation in H_2 (0.74A), the contribution of each H should be very much less than that in H_2. The effects of the hydrogens should be, however, more important than the negative contributions of III and IV, and hence one would expect the combined distortion effects to increase $(\partial^2 V)/(\partial z^2)$ slightly.

For reasons given in a later section it is concluded that structure V contributes 40 to 50 percent to the ground state of the molecule. Hence we conclude that $(\partial^2 V)/(\partial z^2)\approx 0.7\times 10^{15}$ e.s.u. for the borine carbonyl molecule. With the observed couplings this gives 0.06×10^{-24} cm^2 for B^{10} and 0.03×10^{-24} cm^2 for B^{11}. The distortion effects, which we neglect, would tend to decrease these values but not to change their sign, since their estimated total effect is to increase $(\partial^2 V)/(\partial z^2)$.

Magnetic Moments

The nuclear g-factors for both B^{10} and B^{11} have been evaluated by Millman, Kusch, and Rabi[15] with the molecular beam method, and more recently by Bitter[16] using nuclear magnetic resonance. Zimmerman and Williams[17] also give a value for B^{11}/H determined by the magnetic resonance method. Using the frequency ratios given by Bitter, $B^{10}/B^{11}=0.33488$ and $B^{11}/H=0.32085$, with the spin values determined in the present work, one obtains $\mu_{B^{10}}=1.7984$ and $\mu_{B^{11}}=2.6851$ nuclear magnetons. In these calculations we neglect dimagnetic corrections and assume $\mu_H=2.7896$ nuclear magnetons (Table II).

4. MOLECULAR PROPERTIES

From the spacing of the rotational lines for the different transitions it is established that borine carbonyl has a symmetric-top structure. This was indicated by the earlier electron diffraction work of Bauer,[6] but

---

[11] C. H. Townes, Phys. Rev. **71**, 909 (1947); C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

[12] H. A. Bethe and R. F. Bacher, Rev. Mod. Phys. **8**, 226 (1936).

[13] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).

[14] A. Nordsieck, Phys. Rev. **58**, 310 (1940).

[15] Millman, Kusch, and Rabi, Phys. Rev. **56**, 165 (1939).

[16] F. Bitter, Phys. Rev. **75**, 1326(A) (1949).

[17] J. R. Zimmerman and D. Williams, Phys. Rev. **76**, 350 (1949).

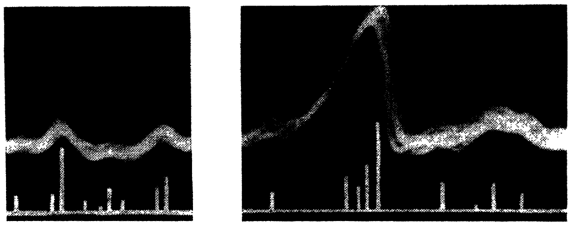

$K=1\rightarrow 1$ $K=0\rightarrow 0$

FIG. 2. A photograph of a cathode-ray tracing of the $J=1\rightarrow 2$ transition of $B^{10}H_3CO$, with bars showing the theoretical spectrum for a nuclear spin of 3 for B^{10}.

small deviations from symmetry cannot be detected by this method.[18] Exclusive of nuclear interactions, the rotational frequencies of a symmetric-top molecule are given by the formula,[19]

$$\nu(\mathrm{cm}^{-1})=2\mathrm{B}(J+1)-2D_{JK}(J+1)K^2-4D_J(J+1)^3$$

where $\mathrm{B}=h/(8\pi^2 cI_{\mathrm{B}})$, and $J=0, 1, 2, \cdots$. Here, I_{B} represents the moment of inertia about an axis perpendicular to the symmetry axis, and D_J and D_{JK} are distortion constants. Values for these constants, except for D_J, as determined from the rotational frequencies are listed in Table III. Although two rotational frequencies were measured for BH_3CO, the constant D_J is so small that its effects were less than the possible error. Its magnitude is apparently less than 10 kc/sec. The D_{JK} values found are rather large, about four times those for methyl bromide and methyl iodide.[20] This indicates that the borine carbonyl bonds are much more easily distorted than are those in the methyl halides.

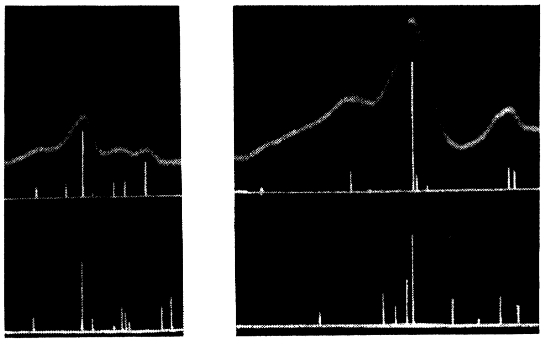

$K=1\rightarrow 1$ $K=0\rightarrow 0$

FIG. 3. A photograph of a cathode-ray tracing of the $J=1\rightarrow 2$ transition of $B^{11}H_3CO$, with bars showing the theoretical spectrum for a nuclear spin of 3/2 (upper) and for a nuclear spin of 5/2 (lower) for B^{11}.

The internuclear distances and bond angles were calculated from the moments of inertia with the equation:

$$I_{\mathrm{B}}=3M_{\mathrm{H}}(x^2+(d^2_{\mathrm{BH}}/2)\sin^2\alpha)+M_{\mathrm{B}}(x-d_{\mathrm{BH}}\cos\alpha)^2 +M_{\mathrm{O}}(d_{\mathrm{BC}}+d_{\mathrm{CO}}-x+d_{\mathrm{BH}}\cos\alpha)^2 +M_{\mathrm{C}}(d_{\mathrm{BC}}-x+d_{\mathrm{BH}}\cos\alpha)^2,$$

where

$$x=\frac{M_{\mathrm{C}}(d_{\mathrm{BC}}+d_{\mathrm{BH}}\cos\alpha)+M_{\mathrm{B}}d_{\mathrm{BH}}\cos\alpha+M_{\mathrm{O}}(d_{\mathrm{BC}}+d_{\mathrm{CO}}+d_{\mathrm{BH}}\cos\alpha)}{3M_{\mathrm{H}}+M_{\mathrm{B}}+M_{\mathrm{O}}+M_{\mathrm{C}}},$$

and where $\alpha=180°-\angle\mathrm{HBC}$. This formula is readily derived from the geometry of the molecule. There are four structural parameters. Hence, the four different isotopic forms studied are just sufficient to determine the structure completely. The interatomic distances and bond lengths obtained are listed in Table IV, with those previously determined from electron diffraction. The accuracy of our values is limited by zero point energy effects. The error limits are not definitely known but are probably less than one percent.

TABLE II. Nuclear moments of boron.

Isotope	Spin I	Quadrupole coupling in BH_3CO $eQ(\partial^2V)/(\partial z^2)$	Quadrupole moment Q	Magnetic moment μ
B^{10}	3	3.36±0.10 mc/sec.	$\sim 0.06\times 10^{-24}$ cm^2	1.7984[a]
B^{11}	3/2	1.55±0.08 mc/sec.	$\sim 0.03\times 10^{-24}$ cm^2	2.7896[a]

[a] Given in nuclear magnetons. These values are determined from Bitter's g-values (reference 16).

The electronic structure of borine carbonyl is rather unusual. To explain the diffraction results of Bauer,[6] Pauling[21] suggested resonance between structures I and

TABLE III. Observed rotational frequencies and molecular constants.

Molecule	ν in mc/sec.[a]	B in mc/sec.	D_{JK} in mc/sec.	I_{B}[b] in g cm^2 $\times 10^{-40}$
$B^{10}H_3C^{12}O$	35,919.74±0.10 ($J=1\rightarrow 2$, $K=0$)	8,979.94	0.39	93.42_{66}
	35,918.17±0.10 ($J=1\rightarrow 2$, $K=1$)			
	53,879.98±0.15 ($J=2\rightarrow 3$, $K=0$)			
	53,877.68±0.15 ($J=2\rightarrow 3$, $K=1$)			
	53,870.70±0.15 ($J=2\rightarrow 3$, $K=2$)			
$B^{11}H_3C^{12}O$	34,628.88±0.10 ($J=1\rightarrow 2$, $K=0$)	8,657.22	0.36	96.90_{92}
	34,627.52±0.10 ($J=1\rightarrow 2$, $K=1$)			
	51,942.84±0.15 ($J=2\rightarrow 3$, $K=0$)			
	51,940.59±0.15 ($J=2\rightarrow 3$, $K=1$)			
	51,934.41±0.15 ($J=2\rightarrow 3$, $K=2$)			
$B^{10}D_3C^{12}O$	30,121.35±0.30 ($J=1\rightarrow 2$, $K=0$)	7,530.34	0.29	111.41_{13}
	30,120.20±0.30 ($J=1\rightarrow 2$, $K=1$)			
$B^{11}D_3C^{12}O$	29,346.26±0.20 ($J=1\rightarrow 2$, $K=0$)	7,336.56	0.24	114.35_{40}
	29.345.33±0.20 ($J=1\rightarrow 2$, $K=1$)			

[a] Frequency here represents the frequency of the rotational line corrected for nuclear quadrupole displacements.
[b] The value for Planck's constant used in calculating I_{B} values is 6.624_2 $\times 10^{-27}$ erg-sec. [from R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941)].

---

[18] The symmetric top configuration is also revealed by the recent infra-red work of R. D. Cowan, J. Chem. Phys. **17**, 218 (1949).

[19] Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. **7**, 509 (1939). G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 224.

[20] Gordy, Simmons, and Smith, Phys. Rev. **74**, 243 (1948).

[21] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), p. 244.

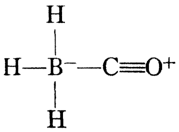
Table IV. Molecular dimensions of borine carbonyl.

	Present value[a]	Electron diffraction value[b]
d_{BH}	1.194A	1.20A
d_{BC}	1.540A	1.57A
d_{CO}	1.131A	1.13A
∠HBH	113°52′	Tetrahedral

[a] The masses used in these calculations are: $M_H=1.00813$, $M_{C^{12}}=12.00386$, $M_O=16.00000$, $M_{B^{10}}=10.01631$, and $M_{B^{11}}=11.01292$, all in a.m.u. [from M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 373 (1937)]. The unit atomic mass used is 1.6599×10^{-24} g [from R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941)].

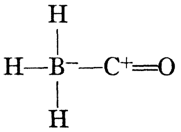
[b] From S. H. Bauer, reference 6.

II. Bauer[6] proposed, in addition, possible contributions



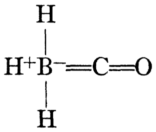
$$\begin{array}{l}\quad\;\mathrm{H}\\ \quad\;|\\ \mathrm{H{-}B^{-}{-}C{\equiv}O^{+}}\\ \quad\;|\\ \quad\;\mathrm{H}\end{array}$$

I.



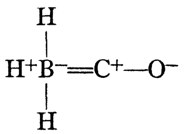
$$\begin{array}{l}\quad\;\mathrm{H}\\ \quad\;|\\ \mathrm{H{-}B^{-}{-}C^{+}{=}O}\\ \quad\;|\\ \quad\;\mathrm{H}\end{array}$$

II.



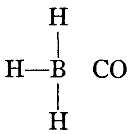
$$\begin{array}{l}\quad\;\mathrm{H}\\ \quad\;|\\ \mathrm{H^{+}B^{-}{=}C{=}O}\\ \quad\;|\\ \quad\;\mathrm{H}\end{array}$$

III.



$$\begin{array}{l}\quad\;\mathrm{H}\\ \quad\;|\\ \mathrm{H^{+}B^{-}{=}C^{+}{-}O^{-}}\\ \quad\;|\\ \quad\;\mathrm{H}\end{array}$$

IV.



$$\begin{array}{l}\quad\;\mathrm{H}\\ \quad\;|\\ \mathrm{H{-}B\quad CO}\\ \quad\;|\\ \quad\;\mathrm{H}\end{array}$$

V.

from structures III and IV. Our results indicate that structure V, which is essentially free BH_3 and CO with no formal bond between B and C, also contributes significantly to the ground state. Contributions from structure V are needed to explain the fact that ∠HBH is intermediate between the tetrahedral *sp*³ type and the planar *sp*² type. If a linear variation of bond type with bond angle is assumed, structure V would contribute about 40 to 50 percent to the ground state of borine carbonyl.

The dipole moment of BH_3CO, which has been measured by Strandberg, Pearsall, and Weiss[8] as 1.795 debye, shows that I and II are not the only important contributing structures. A very large dipole moment is indicated for I or II by the product of the formal charge and the internuclear distances. These are 13 debye for I and 7.3 debye for II. The dipole moment expected for III would be about 1.4 debye in the opposite direction. Structure IV would have a still larger moment in the opposite direction from that of I and II, but from the electronegativity difference of C and O its expected contribution to the ground state would be only about 20 percent that of III. The dipole moment of structure V would be essentially that of carbon monoxide, 0.1 debye. One can account for the observed dipole moment by assuming 40 to 50 percent contribution from V, about 30 percent from I and II combined, and about 20 percent from III and IV combined.

The observed bond lengths are in agreement with the proportional contributions of I to V needed to explain the dipole moment. The BH bonds are of the length expected for normal covalent BH bonds (added radii = 1.20A). The CO length is equivalent to that in carbon monoxide (1.13A). The BC length expected for structure I is 1.66A, the added covalent radii. As pointed out by Pauling,[21] this value should be about 0.10A shorter for II because of the deficit of electrons around C. The contributions from structure V would not influence the BC length significantly because for it there are no electrons in the B orbital along BC. Contributions from structures III and IV would tend to shorten BC, since the added double-bond covalent radii is only 1.43A. However, the CO length expected for the combination of III and IV would be 1.21A (i.e., in CH_2CO and similar molecules), and for this reason large contributions from these structures would not be expected.

From consideration of bond angles, bond lengths, and dipole moments we conclude that borine carbonyl may be considered a resonant hybrid of structures I to V, with their contributions probably decreasing in the order V, II, III, I, and IV. These conclusions are in harmony with the chemical instability of the molecule and with the fact that it can be stabilized under pressure with carbon monoxide.

We wish to thank Vida Miller Gordy for assisting with the calculations and the preparation of the manuscript.

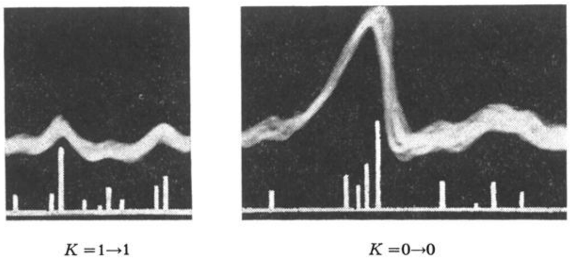
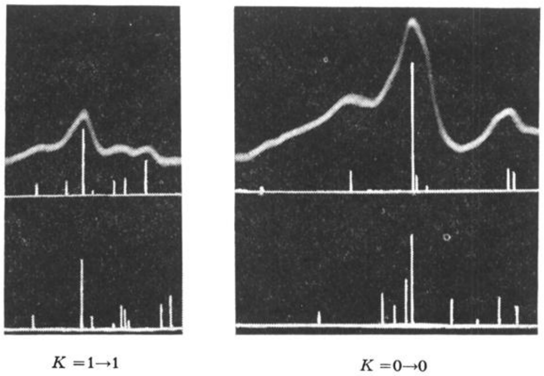

$K=1\rightarrow1$ $K=0\rightarrow0$

FIG. 2. A photograph of a cathode-ray tracing of the $J=1\rightarrow2$ transition of $B^{10}H_3CO$, with bars showing the theoretical spectrum for a nuclear spin of 3 for B^{10}.



$K = 1 \rightarrow 1$ $K = 0 \rightarrow 0$

FIG. 3. A photograph of a cathode-ray tracing of the $J=1\rightarrow 2$ transition of $B^{11}H_3CO$, with bars showing the theoretical spectrum for a nuclear spin of 3/2 (upper) and for a nuclear spin of 5/2 (lower) for B^{11}.