

## MICROWAVE SPECTRUM, STRUCTURE, QUADRUPOLE COUPLING CONSTANTS AND DIPOLE MOMENT OF CARBON MONOXIDE-BORANE

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(Received 23 November 1976)

### ABSTRACT

The  $J = 0 \rightarrow 1$  and  $J = 1 \rightarrow 2$  transitions of thirteen isotopic species of carbon monoxide-borane ( $\text{BH}_3\text{CO}$ ) have been measured. The heavy atom  $r_s$  structural parameters have been calculated in several ways so as to minimize the effects of the small carbon coordinate. The structural parameters found are:  $d(\text{B}-\text{C}) = 1.534 \pm 0.01 \text{ \AA}$ ,  $d(\text{C}-\text{O}) = 1.135 \pm 0.01 \text{ \AA}$ ,  $d(\text{B}-\text{H}) = 1.221 \pm 0.001 \text{ \AA}$ ,  $\angle \text{HBC} = 103.79 \pm 0.06^\circ$ , and  $\angle \text{HBH} = 114.50 \pm 0.15^\circ$ . In addition, a complete  $r_0$  structure has been calculated by least-squares fitting the moments of inertia of all the isotopic species. A dipole moment of  $1.698 \pm 0.02 \text{ D}$  was determined.

### INTRODUCTION

Electron diffraction measurements by Bauer [1] are the earliest structural studies made on carbon monoxide-borane. These measurements established the  $C_{3v}$  symmetry of the molecule and a linear B-C-O arrangement with  $d(\text{B}-\text{C}) = 1.57 \pm 0.03 \text{ \AA}$  and  $d(\text{C}-\text{O}) = 1.13 \pm 0.03 \text{ \AA}$ . Gordy et al. [2] used the microwave spectra of four isotopic species ( $^{10,11}\text{BH}_3\text{CO}$ ,  $^{10,11}\text{BD}_3\text{CO}$ ) to determine the four structural parameters needed to specify the molecular geometry completely. The structure of carbon monoxide-borane has also been re-evaluated by Pépin, Lambert and Cabana using the ground-state rotational constants  $B_0$  obtained from high-resolution IR spectral studies [3-6] of the same species studied by Gordy. They point out that the structural parameters of carbon monoxide-borane cannot be determined accurately by using  $B_0$  from these four isotopic species.

The purpose of this investigation is to re-examine the structure of carbon monoxide-borane using microwave spectral data on thirteen isotopic species. The large number of isotopes available to us made it possible to calculate the bond lengths and bond angles in a number of ways to arrive at independent  $r_s$  and  $r_0$  structures for the  $\text{BH}_3\text{CO}$  molecule. The problem arising from the

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C atom being very close to the center of mass of  $\text{BH}_3\text{CO}$  has been reduced by using the double-substitution procedure [7] to obtain its coordinates.

## EXPERIMENTAL

All compounds were prepared by reacting  $\text{B}_2\text{H}_6$  or  $\text{B}_2\text{D}_6$  with the appropriate species of CO in small stainless steel cylinders at several atmospheres pressure. After several days, the cylinders were cooled to ca.  $-150^\circ\text{C}$  and the unreacted components pumped off. Thereafter, the samples were stored at dry-ice temperatures or below until use. Carbon monoxide enriched in  $^{13}\text{C}$  was supplied by the Los Alamos Scientific Laboratory. The samples prepared from this material contained ca. 6% of  $^{11}\text{BH}_3^{12}\text{C}^{18}\text{O}$  but no evidence for transitions arising from the normal ( $^{12}\text{C}^{16}\text{O}$ ) species could be detected.

Transitions for isotopic species 1 and 2 in Table 1 were measured using the ordinary  $\text{BH}_3\text{CO}$  sample. Those for species 3, 4, 10 and 11 were obtained with the  $^{13}\text{C}$ -enriched sample. The remaining species in Table 1 were obtained from the  $\text{BD}_3\text{CO}$  sample.

All frequency measurements were conducted using cells cooled with dry ice. A conventional Stark spectrometer employing klystrons was used for the  $0 \rightarrow 1$  transitions. An HP 8460A MRR spectrometer was used for the  $1 \rightarrow 2$  transitions. The accuracy of the frequency measurements varied from ca. 0.05 MHz to 0.3 MHz for some of the isotopes seen in natural abundance.

The dipole moment of the molecule was measured on the HP 8460A spectrometer using the  $2 \rightarrow 3$  transition of OCS to calibrate the spectrometer. A value of  $\mu = 0.7152$  D [8] was used for OCS.

TABLE 1

Rotational constants and moments of inertia for various isotopic species of carbon monoxide-borane

Species	Isotope	$B_0$ (MHz)	$I_0$ (uA)
1	$^{11}\text{BH}_3^{12}\text{C}^{16}\text{O}$	$8657.323 \pm 0.052$	58.37555
2	$^{10}\text{BH}_3^{12}\text{C}^{16}\text{O}$	$8980.045 \pm 0.041$	56.27765
3	$^{11}\text{BH}_3^{13}\text{C}^{16}\text{O}$	$8656.415 \pm 0.052$	58.38167
4	$^{10}\text{BH}_3^{13}\text{C}^{16}\text{O}$	$8979.975 \pm 0.041$	56.27811
5	$^{11}\text{BD}_3^{12}\text{C}^{16}\text{O}$	$7336.655 \pm 0.041$	68.88371
6	$^{10}\text{BD}_3^{12}\text{C}^{16}\text{O}$	$7530.328 \pm 0.041$	67.11208
7	$^{11}\text{BD}_3^{13}\text{C}^{16}\text{O}$	$7332.015 \pm 0.091$	68.92730
8	$^{10}\text{BD}_3^{13}\text{C}^{16}\text{O}$	$7526.818 \pm 0.116$	67.14338
9	$^{11}\text{BH}_3^{12}\text{C}^{18}\text{O}$	$8245.397 \pm 0.052$	61.29189
10	$^{10}\text{BH}_3^{12}\text{C}^{18}\text{O}$	$8561.481 \pm 0.052$	59.02904
11	$^{11}\text{BD}_3^{12}\text{C}^{18}\text{O}$	$6981.751 \pm 0.091$	72.38528
12	$^{11}\text{BD}_2\text{H}^{12}\text{C}^{16}\text{O}$	$A_0 = 79892.63 \pm 0.50$ $B_0 = 7802.818 \pm 0.052$ $C_0 = 7623.237 \pm 0.052$	6.32569 64.76839 66.29415
13	$^{10}\text{BD}_2\text{H}^{12}\text{C}^{16}\text{O}$	$A_0 = 79912.16 \pm 0.50$ $B_0 = 8035.230 \pm 0.041$ $C_0 = 7844.210 \pm 0.041$	6.32414 62.89503 64.42663

## ANALYSIS

### Ground-state spectrum

The  $J = 0 \rightarrow 1$  and  $J = 1 \rightarrow 2$  transitions were observed for all the isotopic species except 7, 8, and 10–13, where only the  $J = 1 \rightarrow 2$  lines were detected. The ground-state rotational constants (i.e.  $B_0$ ) for the eleven symmetric isotopic species were obtained by fitting the measured line frequencies to the equation

$$\nu_{J,J+1} = 2B_0(J + 1) - 4D_J(J + 1)^3 - 2D_{JK}(J + 1)K^2 + eqQ \cdot F(I, J, K)$$

The hyperfine structure of the spectral lines associated with the B nucleus could be resolved completely for only a few of the  $J = 0 \rightarrow 1$  transitions. In addition, for the  $J = 1 \rightarrow 2$  transitions, the spectra were further complicated by the presence of the  $K = 1$  lines. The best fit for the rotational frequencies was obtained by using the following values for the three constants  $D_J$ ,  $D_{JK}$ , and  $eqQ$ :  $D_J = 0.005 \pm 0.002$  MHz,  $D_{JK} (^{11}\text{BH}_3) = 0.345 \pm 0.05$  MHz,  $D_{JK} (^{10}\text{BH}_3) = 0.372 \pm 0.05$  MHz,  $D_{JK} (^{10,11}\text{BD}_3) = 0.209 \pm 0.05$  MHz,  $eqQ(^{11}\text{B}) = 1.60 \pm 0.10$  MHz, and  $eqQ(^{10}\text{B}) = 3.45 \pm 0.10$  MHz. Values of the rotational constants (and moments of inertia) are listed in Table 1. It was difficult to obtain accurate results for  $D_J$ , the values of which ranged between 0.003 and 0.006 MHz. Consequently, the value of  $D_J$  listed above was chosen and applied consistently when analyzing all the transitions (except for the asymmetric species where centrifugal distortion was neglected). The values of the constants agree well with those obtained in the previous studies [2–6].

The constants listed above and in Table 1 reproduced the observed center frequencies to 0.04 MHz or better in all cases. A table of the observed and calculated frequencies can be obtained from the British Library Lending Division\* as Sup. pub. no. SUP 26059 (5 pages).

### Structure

The coordinates of the boron and oxygen atoms can be calculated in a number of ways by using Kraitchman's equation for single substitution [9]. The results of three calculations are listed in Table 2; the B–O distance is highly consistent, as expected, since these atoms are far from the center of mass.

When the carbon atom coordinate is calculated, a significant variation is observed in both the B–C and C–O bond lengths. Table 3 shows the results of several calculations using either the single-substitution or the double-substitution equations [7] to calculate the carbon coordinate. The single-substitution calculation of  $d(\text{B–C})$  gives quite short values using  $\text{BH}_3$  parent systems since the carbon atom lies very close to the center of mass. The double-substitution calculation [7] using the  $\text{BH}_3$  species should eliminate this difficulty and is probably the best method to estimate the carbon

\*See *J. Mol. Struct.*, 34 (1976) 322.

TABLE 2

Boron—oxygen bond distances from Kraitchman's equations

Species <sup>a</sup>	Z(B)	Z(O)	d(B—O) (Å)
1, 2, 9	-1.434	1.235	2.669
1, 2, 10	-1.468	1.200	2.668
5, 6, 11	-1.319	1.352	2.671
			av. = 2.669 ± 0.002 Å

<sup>a</sup>Species identified in Table 1. The first species is taken as the parent.

TABLE 3

Boron—carbon bond distances from substitution calculations

Species <sup>a</sup>	Z(B)	Z(C)	d(B—C) (Å)
1, 2, 3, 4 <sup>b</sup>	-1.434	0.100	1.534
5, 6, 7	-1.319	0.211	1.530
6, 5, 8	-1.350	0.179	1.529
1, 2, 3	-1.434	0.079	1.513
2, 1, 4	-1.468	0.022	1.490

<sup>a</sup>Species identified in Table 1. First species identifies the coordinate system.<sup>b</sup>Pierce's method used for first calculation, Kraitchman's equations for the others.

coordinate with the present data. It is also pleasing to observe that the double-substitution calculation results in a  $d(\text{B—C})$  value that is quite close to the value obtained using the  $\text{BD}_3$  species. For the  $\text{BD}_3$  species, the center of mass is shifted significantly so that a single-substitution calculation can be used with more confidence (see Table 3).

The availability of spectral data of the two asymmetric species  $^{11}\text{BD}_2\text{HCO}$  and  $^{10}\text{BD}_2\text{HCO}$  made it possible to use the di-substitution procedure of Li et al. [10] to calculate the  $X$  and  $Z$  coordinates of the in-plane H atom. Two different calculations of these coordinates are listed in Table 4 along with the  $d(\text{B—H})$  bond length and the angles HBC and HBH.

TABLE 4

Boron—hydrogen bond distances from substitution calculations

Species <sup>a</sup>	Z(B)	X(H)	Z(H)	d(B—H)	∠HBH	∠HBC
1, 5, 12	-1.434	1.186	-1.725	1.222	114.50°	103.80°
2, 6, 13	-1.468	1.186	-1.760	1.222	114.51°	103.79°

<sup>a</sup>Species identified in Table 1. The procedure in ref. 10 was used. Axis system defined by the species listed first.

A complete  $r_0$  structure has also been determined by a least-squares fit of the moments of inertia of all thirteen isotopic species using the STRFIT program described by Schwendeman [11].

The best estimates of the  $r_s$  and  $r_0$  structural parameters obtained in this investigation are listed in Table 5. The following considerations were made in choosing the  $r_s$  parameters and their uncertainties. The average value from Table 2 was taken for  $d(\text{B—O})$  plus an uncertainty sufficient to cover the range (about four times the experimental uncertainty). For  $d(\text{B—C})$  and  $d(\text{C—O})$  the value from the first calculation in Table 3 was chosen with an uncertainty derived from experimental uncertainty in the frequency measurements. The uncertainties associated with the  $\text{BH}_3$  parameters are also based on experimental error. The  $r_0$  parameters fitted the observed moments of inertia to 0.01% and the statistical uncertainties from the fitting process are 0.2% or less for the structural parameters. The  $r_s$  structural parameters in Table 5 are preferred since they are expected to be closest to the equilibrium values and probably within 0.01 Å and  $0.5^\circ$  of them.

#### Dipole moment

The Stark coefficients for the  $M = 0$  and  $M = 1$  components of the  $J = 1 \rightarrow 2$ ,  $K = 0$  transition were used to determine the dipole moment of carbon monoxide—borane. The measured values were  $-6.41 \times 10^{-6} \text{ MHz cm}^2 \text{ V}^{-2}$  and  $+5.24 \times 10^{-6} \text{ MHz cm}^2 \text{ V}^{-2}$ , respectively. These gave a dipole moment of  $1.698 \pm 0.02 \text{ D}$ . This value is ca. 6% lower than that reported previously [2] but probably within the uncertainties of that determination.

#### DISCUSSION

Pépin et al. [6] have shown that, owing to the strong correlation that exists between  $d(\text{B—H})$  and  $\angle\text{HBH}$ , an accurate determination of these two structural parameters cannot be made by using spectral data from only the four isotopic species examined in previous microwave studies. This fact accounts for the discrepancies between the values of  $d(\text{B—H})$  and  $\angle\text{HBH}$

TABLE 5

Structural parameters of carbon monoxide—borane

Parameters	$r_s$	$r_0$	$r_0^a$
$d(\text{B—C})$	$1.534 \pm 0.01 \text{ Å}$	1.539 Å	1.540 Å
$d(\text{C—O})$	$1.135 \pm 0.01 \text{ Å}$	1.132 Å	1.131 Å
$d(\text{B—O})$	$2.669 \pm 0.002 \text{ Å}$	2.671 Å	2.671 Å
$d(\text{B—H})$	$1.222 \pm 0.001 \text{ Å}$	1.225 Å	1.196 Å
$\angle\text{HBC}$	$103.8^\circ \pm 0.06^\circ \text{ Å}$	$103.6^\circ$	$104.6^\circ$
$\angle\text{HBH}$	$114.5^\circ \pm 0.15^\circ \text{ Å}$	$114.6^\circ$	$113.9^\circ$

<sup>a</sup>Structural parameters obtained by Gordy et al. [2].

found in this and the earlier microwave investigation (Table 5). Any error due to this correlation has been eliminated in the present work both by direct calculation of the parameters using the di-substitution procedure [10] and also by least-squares fitting the moments of inertia of the thirteen isotopic species. Any suspected ambiguities in  $d(\text{B}-\text{C})$  and  $d(\text{C}-\text{O})$  from the earlier studies, arising from the small carbon coordinate, have also been removed with the additional isotopic data reported here, although the present values for these parameters do not differ markedly from the earlier ones.

The structure of  $\text{BH}_3\text{CO}$  has the following interesting features when compared with other related species. Firstly, the CO distance is practically unchanged from free CO [12]. Secondly, the angle HBX is similar in magnitude to those found in  $\text{BH}_3$  adducts with  $\text{PH}_3$  [13],  $\text{PF}_3$  [14] and  $\text{P}(\text{CH}_3)_3$  [16] but is larger than that found in the trimethylamine adduct [15]. The B-H distance in  $\text{BH}_3\text{CO}$  is also longer by ca. 0.01–0.02 Å than in all of these adducts. Thirdly, the B-C distance appears short when compared with other B-C distances, and this is particularly striking considering the instability of the adduct. Longer B-C distances are found in  $\text{Me}_3\text{B}$  (1.576 Å) [17], tetramethyldiborane (1.59 Å) [18], and in the compound  $\text{Me}_2\text{NBMe}_2$  (1.65 Å) [19]. Shorter B-C bonds occur in  $\text{HCCBF}_2$  (1.513 Å) [20] and  $\text{H}_2\text{CCHBF}_2$  (1.533 Å) [21], but in both the last two cases the carbon atom is part of a  $\pi$  system in which the electrons can also be delocalized onto the boron. For the dissociation of the adduct,  $\Delta H = 4.3$  kcal for the reaction  $\text{BH}_3\text{CO} (\text{g}) \rightarrow 1/2 \text{B}_2\text{H}_6 (\text{g}) + \text{CO} (\text{g})$ , which places it in a category with other very weak adducts such as  $\text{F}_3\text{P}:\text{BH}_3$  [16] and  $\text{Me}_3\text{B}:\text{NMe}_3$  [22, 23]. It is of interest to note that the dative bond distance in the  $\text{F}_3\text{P}:\text{BH}_3$  complex also is unusually short even though the stability of the complex is comparable to that of  $\text{BH}_3\text{CO}$ .

The present results may be examined in the light of a recent extensive MO analysis by Ermler et al. [24]. They find, as might be expected, that the salient feature in the bonding between the donor and acceptor portions of the complex is that the carbon donates a lone pair of electrons to boron in a typical dative bond. However, their calculations do show some back-contribution of electrons from the  $\text{BH}_3$  moiety into a  $\pi$  orbital of the CO (hyperconjugation) which they consider important to the binding. Such a back-donation was suggested some time ago by Graham and Stone [25] to account for the unexpected stability of  $\text{BH}_3$  adducts with very weak bases such as  $\text{PF}_3$  and CO. However, there has been very little, if any, direct experimental evidence supporting such a bonding scheme and the suggestion has received a certain amount of criticism. Alternative suggestions for the stability of these complexes have been based on a polarizability model [26]. Taking all bonding contributions into account, Ermler et al. conclude that the B-C bond is less than half as strong as the B-H bond, which they consider a reasonably normal single bond. They further find that the B-C bond essentially has the appearance of a distorted carbon lone pair when compared with free CO. This conclusion, along with the orbital energy and population analysis, serves to delineate that the C-O bond distance should not differ much from free CO.

as a result of complexation. The most refined wave function used in their calculation predicts a dipole moment of 1.81 D and a boron-11 coupling constant of 2.13 MHz, which overestimates the experimental values by 7% and 33%, respectively.

#### ACKNOWLEDGEMENTS

This work was partially supported by grant No. MPS73-08776 A02 from the National Science Foundation. The authors are indebted to Dr. Robert T. Paine, Jr., of the University of New Mexico, who prepared the samples.

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