

[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION, PASADENA, CALIFORNIA]

The Carborane Series:  $B_nC_2H_{n+2}$ . I.  $B_3C_2H_5$ <sup>1</sup>BY I. SHAPIRO,<sup>2</sup> C. DAVID GOOD AND ROBERT E. WILLIAMS

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An unusual series of compounds corresponding to the empirical formula  $B_nC_2H_{n+2}$ , and termed "carborane-n," has been prepared from pentaborane-9 and acetylene in a silent discharge apparatus. The structure of  $B_3C_2H_5$ , the simplest member of the series thus far observed, has been determined by means of nuclear magnetic resonance, infrared, and mass spectral analyses of isotopic variants of the compound. Some of the physical and chemical properties of carborane-3 ( $B_3C_2H_5$ ) are given.

As far back as 1953, the examination of the mass spectra of a mixture of products from the reaction of diborane with acetylene revealed among others<sup>3</sup> the existence of compounds which had empirical formulas  $B_3C_2H_x$ ,  $B_4C_2H_x$ ,  $B_5C_2H_x$ ; the precise number of hydrogen atoms in the compounds could not be determined with certainty. Somewhat later, mass spectra were obtained of a  $B_4C_2H_x$  and a  $B_5C_2H_x$  from the reaction of pentaborane and acetylene in a silent discharge tube<sup>4</sup>; however, these mass spectra were complicated by the presence of other materials.

Refinement of the separation techniques of the compounds formed in the synthesis<sup>4</sup> and subsequent structural analysis revealed the presence of two compounds with empirical formula  $B_4C_2H_6$ , at least one  $B_5C_2H_7$ , and a small amount of  $B_3C_2H_5$ . Since  $B_3C_2H_5$  was the simplest member of the series, it was purified and investigated first. The other members of the series will be reported later.

## Experimental

**Materials.**—The deuterioacetylene was prepared from the reaction of deuterium oxide and calcium carbide. Deuteriopentaborane was prepared by the pyrolysis of deuteriodiborane as previously described.<sup>5</sup>

**Apparatus.**—The silent discharge apparatus was essentially the same as that described by Stock and Mäthing.<sup>6</sup> A Consolidated Model 21-103 Mass Spectrometer operating at 70 volts was used to obtain the mass spectra. A Perkin-Elmer Model 21 Infrared Spectrophotometer equipped with NaCl optics was used to obtain the infrared spectra. A Varian Model V-4300-2 Nuclear Magnetic Resonance Spectrometer operating at 12.3 and 40 mc., was used to obtain the n.m.r. spectra.

Vapor pressure measurements were made with a vapor tensimeter<sup>7</sup>; temperatures were measured with vapor pressure thermometers ( $NH_3$ ,  $SO_2$ ,  $CO_2$ ,  $C_2H_4$ ). The melting point was determined by Stock's ring method.<sup>8</sup> Standard high vacuum apparatus and techniques were employed where applicable.

**Procedure.**—An equimolar mixture of pentaborane-9 and acetylene (25 mmoles) was circulated through the silent discharge apparatus (15 kv.) for one hour at ambient temperature (the temperature of the reactor increased noticeably during the course of the experiment). During this time, the total pressure of the system gradually decreased,

and a light yellow-brown deposit formed on the walls of the reactor. After the high-voltage discharge was discontinued, the condensable products were transferred to a fractionation train in the high vacuum apparatus.

The desired product was purified by a series of fractionations with trace quantities of the less volatile products finally being removed at  $-126^\circ$ , and the more volatiles, at  $-132$  to  $-135^\circ$ . It was found very difficult to remove traces of biacetylene from the product by means of fractional condensation. However, after storage of the compound at room temperature for a number of weeks, the biacetylene disappeared completely—presumably by polymerization. The purity of the product was monitored by infrared analysis during the various stages of purification.

The yield of  $B_3C_2H_5$  per run was ca. 0.1–0.2%; no study to increase the yield of product was carried out inasmuch as the quantity accumulated from a series of experiments was sufficient for the analyses described here.

## Results

**Spectral Analysis. Mass Spectra.**—The parent grouping in the mass spectra of the various isotopic species<sup>9</sup> of  $B_3C_2H_5$  is illustrated in Fig. 1 and the complete polyisotopic mass spectra of  $B_3C_2H_5$  and  $B_3C_2D_3H_2$  are given in Table I. The isotopic transformation<sup>10</sup> of the  $B^{10}$ -enriched spectrum (Fig. 1a) to an isotopically-normal spectrum (Fig. 1b) reveals that the compound contains three boron atoms with a sharp cutoff corresponding to the  $B_3C_2H_5^+$  species. Additionally, the polyisotopic spectrum of  $B_3C_2H_5$  reduces to the mono-isotopic spectrum with negligible residues when three boron atoms are assumed, and the value of the  $m/e$  63 peak caused by the  $C^{13}$  isotope in normal carbon is in agreement with two carbons per molecule.

The shift upwards by five mass units upon complete deuteration (Fig. 1c) indicates the presence of at least five hydrogen (or deuterium) atoms. Mass spectra cannot be relied upon to show the total number of hydrogen atoms present in boranes.<sup>11</sup> However, the n.m.r. studies described here indicate that the molecular compound contains not more than five hydrogen atoms, hence the empirical formula of the compound is  $B_3C_2H_5$ .

Mass spectral analysis of the exchange reaction of  $B_3C_2H_5$  and  $B_2D_6$  indicates the deuteration of only three hydrogen atoms ( $B_3C_2D_3H_2$ ) to correspond to the product obtained from  $B_5D_9$  and  $C_2H_2$  (Fig. 1d). Interestingly, the product pre-

(1) Presented at the 140th Meeting of the American Chemical Society, Chicago, Illinois, September 1961.

(2) Universal Chemical Systems, Inc., Culver City, California.

(3) H. Landesman and I. Shapiro, to be published.

(4) This experimental work was performed by Dr. B. Keilin in this Laboratory.

(5) I. Shapiro and J. F. Ditter, *J. Chem. Phys.*, **26**, 798 (1957).

(6) A. Stock and W. Mäthing, *Ber.*, **69B**, 1469 (1936).

(7) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 785 (1937).

(8) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933.

(9) The  $B^{10}$ -enriched compound was prepared by Dr. H. Landesman by the reaction of  $B^{10}_2H_6$  and  $C_2H_2$ ; the various deuteriated species were isolated from mixtures originally prepared by Dr. B. Keilin.<sup>4</sup>

(10) I. Shapiro, C. O. Wilson, J. F. Ditter and W. J. Lehmann, *Advances in Chem.*, **32**, 127 (1961).

(11) In the case of tetraborane and pentaborane-11, the cutoff peak corresponds to two mass units lower than the corresponding molecular weight of these compounds.

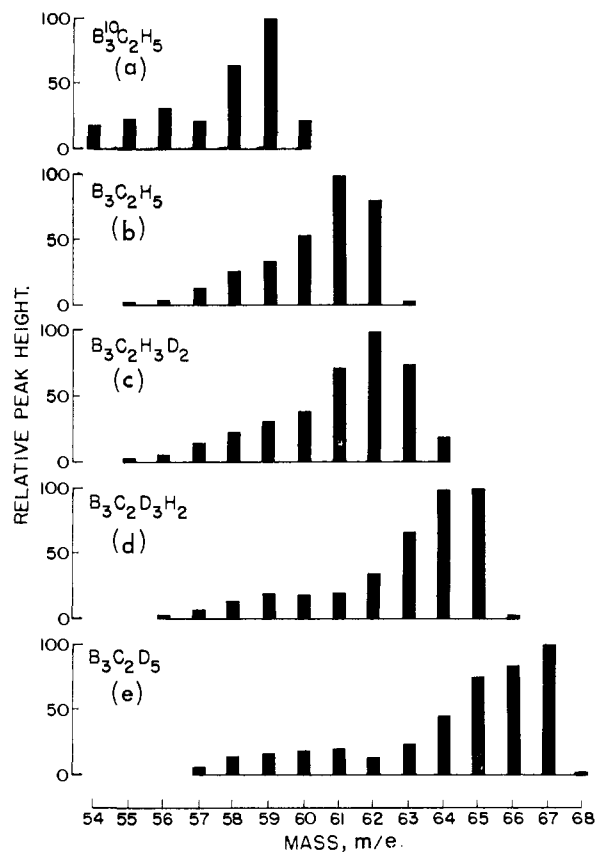


Fig. 1.—Comparison of the parent groupings in the mass spectra of isotopic variants of carborane-3.

pared from the reaction of  $B_5H_9$  and  $C_2D_2$  contains slightly more than two atoms of deuterium (infrared spectra show presence of a small amount of B-D). On the other hand, there are no C-D bonds present in the product formed from  $B_5D_9$  and  $C_2H_2$ . This same phenomenon has been observed in the study of other carboranes. In the case of the mass spectrum given in Figure 1c, the product was exposed to  $B_2H_6$  until the infrared spectrum indicated that all B-D bonds were converted to B-H bonds. For Fig. 1d any trace amount of B-H was removed by repeated exposure of the compound to  $B_2D_6$ .

**Infrared Spectra.**—The infrared absorption frequencies for the various isotopic species of  $B_3C_2H_5$  are given in Table II. The single sharp peak occurring at  $2620\text{ cm}^{-1}$  for  $B_3C_2H_5$  and  $B_3C_2H_3D_2$ , and at  $1973\text{--}1979\text{ cm}^{-1}$  for  $B_3C_2D_3H_2$  and  $B_3C_2D_5$ , indicates a B-H and B-D, respectively, terminal stretching mode.<sup>12,13</sup> This result is compatible with a single hydrogen atom per boron atom, since  $BH_2$  groups in other molecules have always given doublets<sup>14</sup> (symmetric and asymmetric stretching) rather than a singlet. The absence of bands in the region  $1500\text{--}2000\text{ cm}^{-1}$  indicates there are no B-H-B bridge groups.

(12) H. J. Hrostowski and G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 998 (1954).

(13) W. J. Lehmann and I. Shapiro, *Spectrochim. Acta*, **17**, 396 (1961), and references contained therein.

(14) I. Shapiro, C. O. Wilson and W. J. Lehman, *J. Chem. Phys.*, **29**, 237 (1958).

TABLE I

POLYISOTOPIC MASS SPECTRA OF ISOTOPICALLY-NORMAL AND B-DEUTERIATED CARBORANE-3. AVERAGE SENSITIVITY FOR  $B_3C_2H_5$ : 39.2 DIV./ $\mu$  FOR  $m/e$  61 ADJUSTED TO BUTANE SENSITIVITY OF 50 FOR  $m/e$  43

$m/e$	$B_3C_2H_5$ peak ht.	$B_3C_2D_3H_2$ peak ht.	$m/e$	$B_3C_2H_5$ peak ht.	$B_3C_2D_3H_2$ peak ht.
2	0.3	1.8	38	0.1	6.9
4	..	0.1	39		4.5
11	26.5	30.7	40		0.2
12	4.3	2.7	41		.2
13	3.1	6.3	42		.2
14	0.1	2.7	43	0.1	.4
15		1.4	44	.1	.7
16		0.2	45	.7	.6
21	.2	.2	46	2.0	1.3
22	.5	.5	47	3.9	2.4
23	.9	.7	48	4.1	3.4
24	1.6	1.2	49	2.3	3.6
25	2.4	1.7	50	0.9	2.7
26	1.2	3.3	51		1.6
27	0.2	1.3	52		0.5
28	.1	1.5	53		.1
29	.1	0.4	54	.1	.2
29.5	.4	.04	55	.7	.6
30	1.1	.2	56	4.2	2.3
30.5	1.3	0.35	57	14.1	7.0
31		1.0	58	26.4	14.1
31.5		1.3	59	31.4	19.5
32	0.1	0.6	60	53.1	19.1
33	0.6	0.6	61	100	20.3
34	2.0	1.7	62	82.6	35.2
35	3.7	2.8	63	1.8	67.0
36	5.4	4.5	64		99.2
37	6.4	5.4	65		100
			66		2.2

An interesting feature of the infrared spectra is the apparent absence of absorption bands in the vicinity of  $2800\text{ to }3300\text{ cm}^{-1}$  for assignment to a C-H stretching vibration (or  $2000\text{--}2200\text{ cm}^{-1}$  for C-D stretching vibrations),<sup>15</sup> for isotopically-normal carborane-3 pressures up to 123 mm. in a 5 cm. gas cell failed to reveal any absorption in the C-H stretching region. In this connection attention is called to the fact that single C-H absorptions in alkanes and derivatives are known to be extremely weak.<sup>16,17</sup> That the absence of C-H stretching absorptions may be accidental because of near zero dipolar change remains to be determined; a critical analysis of the infrared spectra of carboranes is in progress.

On the basis of a study of the infrared spectra of various organoboranes,<sup>13</sup> a speculative assignment of several of the other frequencies given in Table II can be made:  $1000\text{--}1100\text{ cm}^{-1}$ , B-C stretching;  $780\text{ cm}^{-1}$ , B-B stretching;  $903$  and  $883\text{ cm}^{-1}$ , B-D bending.

**Nuclear Magnetic Resonance Spectra.**—The  $H^1$  and  $B^{11}$  n.m.r. spectra of isotopically-normal

(15) The absence of C-H stretching vibrations in the infrared spectra also has been noted in several other members of the carborane series, e.g.,  $B_4C_2H_8$  and  $B_5C_2H_7$ .

(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1958, p. 15.

(17) J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press, New York, N. Y., 1954, pp. 472-3.

TABLE II  
INFRARED ABSORPTION SPECTRA OF ISOTOPIC VARIANTS  
OF CARBORANE-3

s, strong; m, medium; w, weak; v, very; sh, shoulder;  
b, broad.

$B_3C_2H_5$ , cm. <sup>-1</sup>	$B_3C_2D_3H_2$ , cm. <sup>-1</sup>	$B_3C_2H_3D_2$ , cm. <sup>-1</sup>	$B_3C_2D_5$ , cm. <sup>-1</sup>
2620 vs		2620 vs	
	1985 sh		1989 sh
	1973 vs		1979 vs
	1961 sh		1967 sh
	1751 w		1739 w
1236 m	1216 m	1230 w	
1226 m	1207 m	1220 w	
1217 m	1198 m		1180 w
1205 sh	1187 m		1165 w
	1093 sh	1115 sh	
1119 vs	1088 vs	1104 vs	1034 sh
1108 sh		1090 sh	1028 s
1102 vs	1082 vs	1082 vs	1018 vs
1092 vs	1074 sh	1070 sh	1009 sh
		1052 w	
920 mb		903 m	
910 sh		890 sh	
903 s		883 s	
890 m		868 sh	
	841 m		
	835 m		
	831 m		
	819 sh		
800 wb			
788 w	769 w	785 w	789 m
772 wb	756 w		774 m
			728 w

TABLE III  
VAPOR PRESSURE OF CARBORANE-3

Temp., °C.	V.p. obsd., mm.	V.p. calcd., mm.	Dev., mm.
-95.6	2.4	2.3	-0.1
-89.0	4.4	4.3	- .1
-83.4	7.1	7.0	- .1
-79.0	10.1	10.2	+ .1
-64.6	30.3	30.4	+ .1
-64.5	30.4	30.7	+ .3
-58.5	45.8	46.1	+ .3
-57.3	49.9	49.9	0
-53.8	62.7	62.5	-0.2
-49.6	80.9	80.9	0
-45.4	103.2	103.7	+0.5
-40.2	139.3	139.1	- .2
-38.9	148.6	149.3	+ .7
-37.0	166.1	165.4	- .7
-22.6	338.1	339.2	+1.1
-18.5	410.2	409.3	-0.9
-13.5	510.7	509.8	-0.9

Av. dev. 0.37

<sup>a</sup> All values have been corrected to the density of mercury at 0°.

$B_3C_2H_5$  are given in Fig. 2. The proton spectrum (Fig. 2a) reveals that the protons exist in two

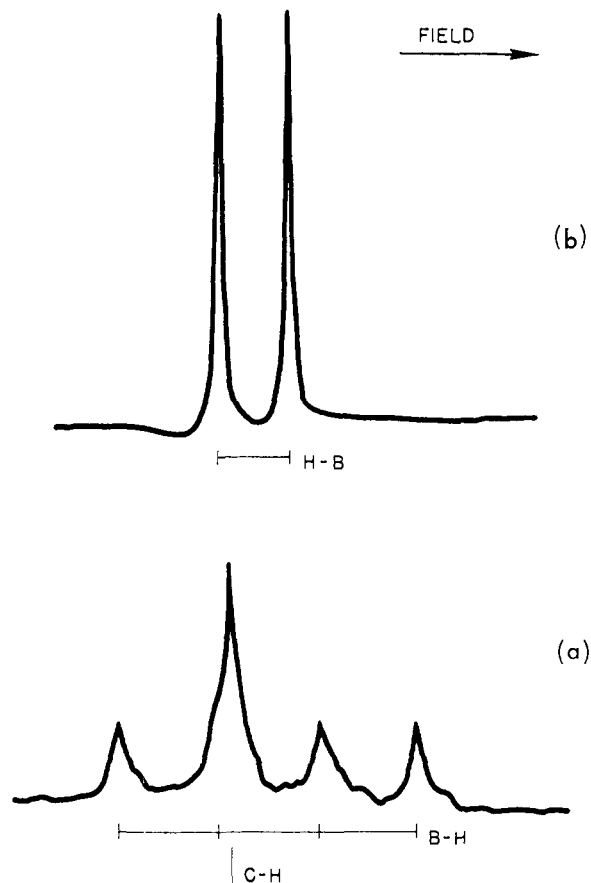


Fig. 2.—Nuclear magnetic resonance spectra of isotopically-normal carborane-3: (a)  $H^1$  spectrum taken at 40 Mc., (b)  $B^{11}$  spectrum taken at 12.3 Mc.

distinct environments—some protons connected to identical carbon atoms (single peak) and others connected to identical boron atoms (quartet peaks).<sup>18,19</sup> The spectra reveal absence of bridge hydrogens. The doublet of the  $B^{11}$  spectrum (Fig. 2b) demonstrates that all boron atoms are spectroscopically equivalent and that there is only one proton attached to each boron atom. The extreme sharpness of the boron spectrum indicates that the field gradient about each boron atom is nearly zero.

**Physical Properties. Vapor Pressure.**—The vapor pressure of spectroscopically pure  $B_3C_2H_5$  was measured over the temperature range of  $-95^\circ$  to  $-13^\circ$  and reported in Table III. Included in this table are the vapor pressure values obtained from the equation

$$\log P_{\text{mm}} = 9.10154 - 1459.18/T - 0.002986T$$

**Boiling Point.**—Extrapolation of the vapor pressure data to one atmosphere pressure gives a normal boiling point of  $-3.7^\circ$ .

**Melting Point.**—Four melting point determinations indicate that the melting point of  $B_3C_2H_5$  is  $-126.40 \pm 0.05^\circ$ .

(18) I. Shapiro, R. E. Williams and S. G. Gibbins, *J. Phys. Chem.*, **65**, 1061 (1961).

(19) R. E. Williams, S. G. Gibbins and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 6164 (1959).

**Heat of Vaporization.**—The molar heat of vaporization at the normal boiling point, calculated from the Clausius-Clapeyron equation, is 5684 cal./mole. Trouton's constant is 21.1 cal./deg. mole, a value consistent with those usually obtained for unassociated compounds.

**Chemical Properties. Stability.**—Essentially no decomposition of  $B_3C_2H_5$  has been observed, even on prolonged storage at room temperature.

**Reactivity.**— $B_3C_2H_5$  has been in contact with acetone, trimethylamine, carbon dioxide, air and water at room temperature without noticeable reaction.

An exchange reaction occurs with deuteriodiborane in which the three hydrogens attached to boron are replaced by deuterium atoms (half-time at room temperature *ca.* 7 hours).

#### Discussion

The combination of information derived from mass spectra and n.m.r. spectra of the product described here dictates a molecular structure consisting of three identical B-H units and two identical C-H units. Although the infrared spectra show no absorption frequencies which can be assigned to a C-H stretching mode, the evidence is strongly in favor of the existence of two C-H units.

The mass spectral fragmentation pattern of  $B_3C_2H_5$  indicates that most fragments result from a loss of hydrogens rather than a breaking of the boron-carbon skeleton and, as such, is more akin to aromatics, *e.g.*, benzene, rather than to aliphatics, *e.g.*, hexane or even cyclohexane. This stability may be attributed to resonance.

Based on the above considerations, the most probable structure for the  $B_3C_2H_5$  molecule is a trigonal bipyramid in which the three boron and associated hydrogen atoms lie in one plane with the two carbons and their hydrogen atoms lying along the axis perpendicular to the equilateral triangle formed by the boron atoms, and occupying apical position, *i.e.*, the carbon atoms lie on opposite sides of the boron plane. This structure is compatible with the small number of fundamental bands observed in the infrared spectrum.

$B_3C_2H_5$  has been formed as one of the reaction products of acetylene and pentaborane. No doubt the mechanism of such reaction is complex; however, the hydrogens originally attached to the borons and carbons are primarily retained in the new structure.

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### Cyclic Organodiboranes: 1,2-Tetramethylenediborane and 1,2-(1'-Methyltrimethylene)-diborane

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Two compounds having the empirical formula  $B_2C_4H_{12}$  were prepared by the reaction of butadiene and diborane. These compounds have been characterized as the cyclic organodiboranes: 1,2-tetramethylenediborane and 1,2-(1'-methyltrimethylene)-diborane by means of their mass, infrared and n.m.r. spectra and by analysis of their oxidation products.

#### Introduction

The reaction between diborane and 1,3-butadiene has been reported by Köster<sup>2,3</sup> and also by Zweifel, Nagase and Brown,<sup>4</sup> and a possible conflict<sup>4</sup> has arisen regarding products of the reaction.<sup>2,3</sup> Köster has reported the isolation of 1,1'-tetramethylene-bis-borolene,  $B_2(C_4H_8)_2$ , and bisborocyclopentene,  $C_4H_8BH_2BC_4H_8$ , as products of the reaction. All reported compounds have boron attached at the 1,4-positions in butadiene. Brown and co-workers, on the other hand, report the reaction product to be polymeric, having average molecular weights of 320 to 365. Interestingly, oxidation of this product was reported to yield substantial amounts of the 1,3-diols, thus indicating like substitution in the original

borane polymer. The reaction conditions reported in the separate papers are different, however, Köster having used trialkylamineboranes with butadiene at 0° to 25°, while Brown's group utilized tetrahydrofuran solutions of diborane at room temperature. In both cases a borane adduct was used as one of the reactants.

In our laboratory, the reactions between diborane and 1,3-butadiene were studied under still other conditions, *i.e.*, in the vapor phase at 100° with only hydrogen as a diluent. Under these conditions the product contained, in addition to polymeric materials, an appreciable amount of the 1:1 butadiene-diborane addition product. Analysis of the product revealed it to be primarily 1,2-tetramethylenediborane, containing also small amounts of 1,2-(1'-methyltrimethylene)-diborane. The compounds are unique in that they incorporate the double-hydrogen bridge of the diborane molecule into a single cyclic organoborane compound. Assuming the reported work of the previous authors<sup>2,3,4</sup> to be correct, it appears that the

(1) (a) Dynamic Science Corp., South Pasadena, Calif. (b) Aerospace Corp., Los Angeles 45, Calif. (c) Universal Chemical Systems, Inc., Culver City, Calif.

(2) R. Köster, *Angew. Chem.*, **71**, 520 (1959).

(3) R. Köster, *ibid.*, **72**, 626 (1960).

(4) G. Zweifel, K. Nagase and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183 (1962).