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$C_2B_6H_{10}$, A NEW nido-CARBORANE; CORRELATION OF EIGHT-VERTEX nido- AND arachno-STRUCTURES

by

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13 ABSTRACT

A new carborane has been prepared by the gas phase reaction of $1,5\text{-}C_2B_3H_5$ and diborane at 300° in a flow system. The mass spectral cut-off and profile show it to be a nido-carborane with the empirical formula $C_2B_6H_{10}$, while 32-MHz ^{11}B nmr analyses show that it is not a conventional nido-compound but has instead an open arachno-structure (as does its isoelectronic analog B_8H_{12}) in which the carbons are opposite one another in the 4,7-positions in the open mouth and the bridge hydrogens are also opposite each other joining the 5,6- and the 3,8-positions (B_8H_{12} numbering system). The fact that it has this structure implies that bridge hydrogen placement may be the most important feature in the structuring of boranes and carboranes.

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$C_2B_6H_{10}$, A NEW *nido*-CARBORANE; CORRELATION OF EIGHT-VERTEX *nido*- AND *arachno*-STRUCTURES

By Alan J. Gotcher,[1,2] Robert E. Williams,[2] and J. F. Ditter[2]

A new carborane has been prepared by the gas phase reaction of 1,5-$C_2B_3H_5$ and diborane at 300° in a flow system. The mass spectral cut-off and profile show it to be a *nido*-carborane with the empirical formula $C_2B_6H_{10}$, while 32-MHz ^{11}B nmr analyses show that it is not a conventional *nido*-compound but has instead an open *arachno*-structure (as does its isoelectronic analog B_8H_{12}) in which the carbons are opposite one another in the 4,7-positions in the open mouth and the bridge hydrogens are also opposite each other joining the 5,6- and the 3,8-positions (B_8H_{12} numbering system). The fact that it has this structure implies that bridge hydrogen placement may be the most important feature in the structuring of boranes and carboranes.

In the course of experimental studies[3] involving gas phase reactions between the small *closo*-carboranes and boron hydrides, with the expectation of synthesizing larger carborane molecules such as $C_2B_6H_8$, $C_2B_7H_9$, and $C_2B_8H_{10}$ as precursors for carborane-siloxane polymers,[4] a new *nido*-carborane, $C_2B_6H_{10}$ was discovered among a variety of other carborane products. This molecule was of interest first from a structural standpoint because its isoelectronic *nido*-borane analog, B_8H_{12}, uniquely assumes an *arachno*-configuration[5] (resembling the skeletal structure of non-isoelectronic B_8H_{14}), and second it was of practical interest as a possible source of $C_2B_6H_8$. For these reasons we prepared a sufficient quantity of $C_2B_6H_{10}$ for structural characterization as well for a study of its decomposition characteristics.

The nido-carboranes are categorized according to the empirical formula $C_{0-4}B_nH_{n+4}$, and known compounds to date include the pentagonal pyramid series B_6H_{10}, CB_5H_9, $C_2B_4H_8$, $C_3B_3H_7$ and $C_4B_2H_6$[6] as well as the following members of other series: $C_2B_3H_7$,[7] $C_2B_7H_{11}$,[8] and two isomers each of $C_2B_8H_{12}$,[8,9] and $C_2B_9H_{13}$.[10]

Other reported gas phase reactions between boranes and carboranes include that of diborane with 4,5-$C_2B_4H_8$,[11] which gives myriad higher molecular weight carboranes and their derivatives, the reaction of diborane with 1,3-$C_2B_7H_{13}$,[12] which yields predominantly $C_2B_8H_{10}$, and the reaction of pentaborane-9 with $C_2B_3H_5$,[3] which also produces $C_2B_8H_{10}$.

Experimental Section

Reagents. The reagents used to prepare $C_2B_6H_{10}$ consisted of diborane, obtained from Callery Chemical Company, and the closo-carborane 1,5-$C_2B_3H_5$, which was synthesized by the reaction of pentaborane-9 with acetylene[13] and subsequently obtained pure by gas chromatographic fractionation of the closo-carborane product mixture generated in the pentaborane-9/acetylene reaction.

Experimental Conditions and Apparatus. Reaction conditions consisted of a flow system (~20 seconds nominal residence time) of equimolar quantities of diborane and $C_2B_3H_5$ at one-half atmosphere in a 0.75-in. X 12-in. stainless steel tube reactor heated to 300°. The effluent from the reactor was sampled intermittently and analyzed by a gas chromatograph coupled to a mass spectrometer. The condensable products were collected in a liquid nitrogen cooled trap, and the combined product from several such preparations was subsequently purified in one pass on a large scale (2-in. diameter X 15-ft. long) chromatographic column of Apiezon N on

Chromosorb P. Approximately 1.9 grams of GC-pure $C_2B_6H_{10}$ was obtained in this manner.

Reaction and Products. In the thermal decomposition of diborane one of the transient products is generally conceded to be B_3H_7, present in pseudo-equilibrium with B_2H_6,[14] and since diborane is thermally much less stable than $C_2B_3H_5$ a plausible mechanism for formation of $C_2B_6H_{10}$ is the reaction

$$C_2B_3H_5 + [B_3H_7] \longrightarrow C_2B_6H_{10} + H_2. \quad (1)$$

The results of four analyses of the products of the $C_2B_3H_5$/diborane reaction at 300° are shown in Table 1. At slightly higher reaction temperatures the ratio of $C_2B_6H_8$ to $C_2B_6H_{10}$ was observed to increase proportionately with the temperature increase, suggesting that $C_2B_6H_8$ evolves from $C_2B_6H_{10}$ by simple loss of hydrogen, i.e.,

$$C_2B_6H_{10} \longrightarrow C_2B_6H_8 + H_2. \quad (2)$$

$C_2B_5H_7$ and $CH_3CB_5H_8$, other major products in the diborane/$C_2B_3H_5$ reaction, are probably formed by direct assimilation of B_2H_6 by $C_2B_3H_5$, i.e.,

$$C_2B_3H_5 + B_2H_6 \longrightarrow CH_3CB_5H_8 \quad (3)$$

$$C_2B_3H_5 + B_2H_6 \longrightarrow C_2B_5H_7 + 2H_2 \quad (4)$$

$C_2B_6H_{10}$ is an air sensitive clear liquid which is relatively unstable in the liquid phase, decomposing at ambient temperatures primarily to $C_2B_6H_8$ and $C_2B_5H_7$, as shown in Table 2. However, it can be stored in the gas phase for extended periods of time with no apparent decomposition. The formation of $C_2B_6H_8$ can be ascribed to reaction (2), while $C_2B_5H_7$ could arise by loss of BH_3 from $C_2B_6H_{10}$.

Structural Characterization

Mass Spectra. The polyisotopic mass spectrum of the envelope of the parent peaks of $C_2B_6H_{10}$ shown in Table 3 has a cut-off at m/e 100, corresponding to the ion $^{12}C_2{}^{11}B_6H_{10}{}^+$, and has its maximum intensity peak at m/e 96. The calculated monoisotopic spectrum (also shown in Table 3) indicates that $C_2B_6H_8{}^+$ (closo-fragment) is the most stable ion species, as one would expect from a comparison of the stabilities of the closo- and nido-structures.[15] The mass spectral profile[15] is typically that of a nido-carborane.

Infrared Spectra. Infrared absorption bands are as follows: 1351 (vb), 1412 (m), 1446 (m), 1449 (m), 1457 (m), 1466 (m), 1508 (w), 1880 (w), 1710 (w), 1725 (w), 1732 (w), 1952 (w), 2603 (s), 2865 (s), 2878 (w), 2965 (w), and 2975 (w).

Nmr Spectra. The structure of $C_2B_6H_{10}$, I, is presented in Figure 1 and deduced with ease from the ^{11}B nmr spectrum (a, b, c of Figure 2). From the apparent 4:2 doublet pattern, the doublet of area 2 at higher field is attributed to the higher-coordinated boron atoms in the cage, while the doublet at lower field is due to the four lower-coordinated edge borons.[6a] The doublet at lower field was further split as the temperature of the sample was increased, clearly showing the anticipated coupling between the boron atoms and the bridge hydrogen atoms. This coupling substantiates the open, non-adjacent bridge structure, for in all cases thus far studied where a boron atom is associated with one and only one bridge hydrogen and tautomerism is absent, a 20-50 c/s boron-to-bridge-hydrogen coupling has been observed.[6a] The ^1H nmr spectrum (Figure 3) is completely compatible with and reinforces the structure presented in Figure 1.

Using the numbering system for B_8H_{12},[16] the bridge hydrogens in $C_2B_6H_{10}$ join the 5,6- and the 3,8-positions, while the carbons occupy the 4,7-positions. Its formal name therefore is 4,7-dicarba-nido-hexaborane (10).

Discussion of Structures

The structures of all the known nido-carboranes and boranes have been depicted as polyhedral fragments derived by the formal removal of a high coordination vertex from the appropriate closo-carborane,[17] although in some cases the nido-fragment opens to an arachno-structure by the breaking of one additional bond. For example, the skeletal structure of the $B_6H_{10} \ldots C_4B_2H_6$ series is produced by removing the highest coordination vertex from the closo-carborane $C_2B_5H_7$, whereas the $B_8H_{12} \ldots C_4B_4H_8$ series is derived from $C_2B_7H_9$ (II in Figure 1) but with the additional bond being ruptured in every known member of this series.

All nido-structures that have previously been characterized have their bridge hydrogens (when present) around the open face, and all nido-carboranes except $C_2B_3H_7$ also have their carbon atoms about the open face. All but two nido-carboranes (an isomer of $C_2B_8H_{12}$ and one of $C_2B_9H_{13}$) have their carbon atoms located adjacent to each other.

However, as is evident from its nmr spectrum the structure of $C_2B_6H_{10}$ deviates from the "norm" in that it is not a true nido-carborane but is instead an open or pseudo-arachno type. Hence, it resembles its isoelectronic borane counterpart, B_8H_{12} (III in Figure 4), which even though it is a nido-borane according to its empirical formula, has an open arachno-structure in the crystalline state all of the time and in the liquid phase most of the time. The cause of this apparent anomaly in the case of B_8H_{12}

may possibly be due to the lack of space needed to accommodate the bridge hydrogens in the lowest coordination positions around the five-membered open face of the molecule. Lipscomb has remarked that the skeletal atoms and the bridge hydrogens in the boranes and carboranes are placed roughly on the surface of an inner sphere while the terminal hydrogens are roughly placed on the surface of an outer sphere. In this fashion one can appreciate that the four bridge hydrogens in a nido-structured B_8H_{12} molecule would be more crowded than they would be in B_5H_9 or B_6H_{10}.

If the pseudo-arachno-$C_2B_6H_{10}$ had had adjacent carbon atoms (V in Figure 1) a true nido-structure might have been observed since then the two bridging hydrogens would have had sufficient room. This was not to be the case, however, and only the direct structural analog (I) of B_8H_{12} (III) was observed.

Therefore, the fact that $C_2B_6H_{10}$ and B_8H_{12} have arachno- rather than nido-structures suggests that nido-structures prevail where adequate room for the bridge hydrogens is available, e.g., B_5H_9, B_6H_{10}, and $B_{10}H_{14}$ and their derivatives, but arachno-structures dominate where there is not enough room, as in $C_2B_6H_{10}$ and in the B_8H_{12} open structure, which is similar to but not isoelectronic with that of B_8H_{14} (XIII in Figure 4). On the other hand, as the number of bridge hydrogens diminishes, i.e., are supplanted by the appropriate number and proper placement of carbon atoms, the "bridge hydrogen accommodation" problem becomes less severe and the existence of true nido-configurations becomes increasingly more probable (VI and VII in Figure 1). This bridge hydrogen crowding problem could also explain why nido-boranes such as B_3H_7, B_4H_8, B_7H_{11} and B_9H_{13} have never been observed as stable compounds.

One observation that lends some credence to this nido- vs. arachno- thesis is the fact that Lewis bases are known to improve the stabilities of certain of the more tenuous *nido*-structures, suggesting that here the Lewis base promotes a structural transformation from a *nido*- to an *arachno*-configuration and therefore insures ample accommodation of the bridge hydrogens. The *nido*-boranes B_5H_9 and $B_{10}H_{14}$, for example, can accommodate four bridge hydrogens with ease, and they undergo no apparent enhancement in stability from the presence of weak Lewis bases, while two *nido*-boranes of lesser stability, B_6H_{10}[18] and B_2H_6,[19] are definitely stabilized by the weak Lewis bases cineole and tetrahydrofuran, respectively. Furthermore, the still less stable *nido*-borane, B_8H_{12}, with its *arachno*-structure, complexes readily with weak Lewis bases to form true *arachno*-borane adducts, i.e., B_8H_{12}:OEt_2 (X in Figure 4) and B_8H_{12}:$NCCH_3$.[5] Although B_9H_{13} has never been observed, the C,C'-dimethyl derivative of $C_2B_7H_{11}$ (which is isoelectronic with B_9H_{13}) assumes the *arachno*-structure of B_9H_{15}.[8] This suggests that a *nido*-B_9H_{13} with an *arachno*-structure may one day be isolated.

Finally, B_3H_7, B_4H_8, and B_9H_{13} so far have been found to be stable only as *arachno*-borane Lewis base adducts, i.e., B_3H_7:OEt_2,[20] B_4H_8:CO,[21] and B_9H_{13}:$NCCH_3$.[22] B_7H_{11}, perhaps the least stable *nido*-borane of all, has never been observed (except perhaps transiently)[23] either neat or as an adduct.

We have presumed that B_8H_{12}, III, opens up because of bridge hydrogen crowding. However, since the isoelectronic $C_2B_6H_{10}$ carborane, with only two bridge hydrogens, also has an *arachno*-structure (and therefore presumably has a less severe crowding problem) it is conceivable that the eight-vertex *arachno*-structure is not much less stable, if any, than the eight vertex *nido*-structure. Perhaps only isoelectronic anions such as $B_8H_{10}^{2-}$, VIII, or $C_2B_6H_8^{2-}$, IX (both have *nido*-empirical formulae), can exist in *nido*-configurations since here there would be no bridge hydrogen crowding and no carbons in high coordination positions susceptible to transformation into an *arachno*-borane structure.

In excess ether the intramolecular exchange of four bridge hydrogens and the intermolecular exchange of ether molecules in B_8H_{12}:OEt_2 (X in Figure 4) is revealed by the symmetrical doublets and by the shift to higher field of the doublet representing the low-coordinated edge positions. This behavior has a precedent in B_3H_7:OEt_2 which in excess ether displays a symmetrical multiplet in its ^{11}B nmr spectrum,[21] indicating that all of the hydrogens are engaged in rapid intramolecular exchange (i.e., tautomerism) and that ether molecules are sequentially complexing with various borons. As is the case with both B_8H_{12} and B_3H_7 the introduction of a stronger Lewis base generates a static molecule by terminating Lewis base exchange and consequently quenching tautomerism. That these strong Lewis base adducts are static is revealed by the appearance of many different kinds of borons in the ^{11}B nmr spectra[5] of B_8H_{12}:$NCCH_3$ and $B_8H_{12}N(CH_3)_3$, XII, and the appearance of two kinds of boron in B_3H_7:PF_3.[24]

The ^{11}B nmr spectrum[5] of B_8H_{12}, III, reveals two doublets of equal intensity representing four borons each (4:4). This is incompatible with the X-ray structure (III in Figure 1) which would presuppose five doublets in the ratio of 2:2:2:1:1 or three doublets in the ratio of 4:2:2, as would be anticipated in a system involving bridge hydrogen tautomerism about the open face. The mechanism we prefer is displayed in Figure 1. It incorporates an _arachno_ to _nido_ to _arachno_ rearrangement which allows the 4:2:2 spectrum from bridge hydrogen tautomerism to become a 4:4 spectrum since the _nido_-intermediate allows each of the two sets of two borons to become equivalent. We suggest that a transient _nido_-configuration (bridge hydrogen crowded) intermediate III in Figure 1, which facilitates the cage-edge boron equivalence in B_8H_{12}, is unavailable to B_8H_{14}, XIII in Figure 4.

The arachno-borane, B_8H_{14} (XIII in Figure 4), with six extra tautomerizing hydrogens, has three kinds of boron in the ratio of 4:2:2 because no cage-edge skeletal rearrangement mechanism is available. For completeness another isoelectronic analog of B_8H_{14}, e.g., $R_2NB_8H_{11}:NR_3$, XI, is shown in Figure 4.

In conclusion, while the data distinctly favor the arachno-structure for $C_2B_6H_{10}$, the pair of valence bond tautomers, IV and IV' in Figure 1 should not be completely ruled out. The necessity of a transient nido-B_8H_{12} intermediate (III in Figure 1) to account for its ^{11}B nmr spectrum would argue for such nido-valence bond tautomers (V) for $C_2B_6H_{10}$, while the lack of evidence for hydrogen tautomerism and the "distaste" of carbon for cage positions in the nido- and arachno-carboranes argue against the existence of IV and IV'.

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TABLE I

PRODUCTS OF THE REACTION BETWEEN B_2H_6 AND $C_2B_3H_5$ AT 300°

Compound	Product Distribution #1	#2	#3	#4
B_4H_{10}	T	T	T	T
1,5-$C_2B_3H_5$	24.6	35.4	43.9	57.4
1,6-$C_2B_4H_6$	5.9	2.2	1.8	2.2
2,4-$C_2B_5H_7$	45.9	17.7	11.0	15.7
$(CH_3)_2C_2B_3H_3$	T	T	T	T
$CH_3C_2B_4H_5$	T	T	T	T
$C_2B_6H_8$	3.2	5.7	5.9	3.6
$CH_3CB_5H_8$	1.1	12.7	14.7	7.6
m/e 90	6.0	11.7	10.4	7.0
m/e 86	T	T	T	T
$C_2B_6H_{10}$	7.8	14.5	12.2	6.4
$C_2B_7H_9$	0.5	T	---	---
1,10-$C_2B_8H_{10}$	5.0	T	---	---
$(C_2B_3H_4)_2$	T	T	---	---

TABLE II

PRODUCTS FORMED FROM THE ROOM TEMPERATURE DECOMPOSITION OF $C_2B_6H_{10}$

Compound	Percent
$C_2B_6H_{10}$	26.0
m/e 90	1.2
$CH_3CB_5H_8$	7.7
$C_2B_6H_8$	25.4
$C_2B_5H_7$	29.0
?	4.6
$C_2B_3H_5$	6.1

TABLE III

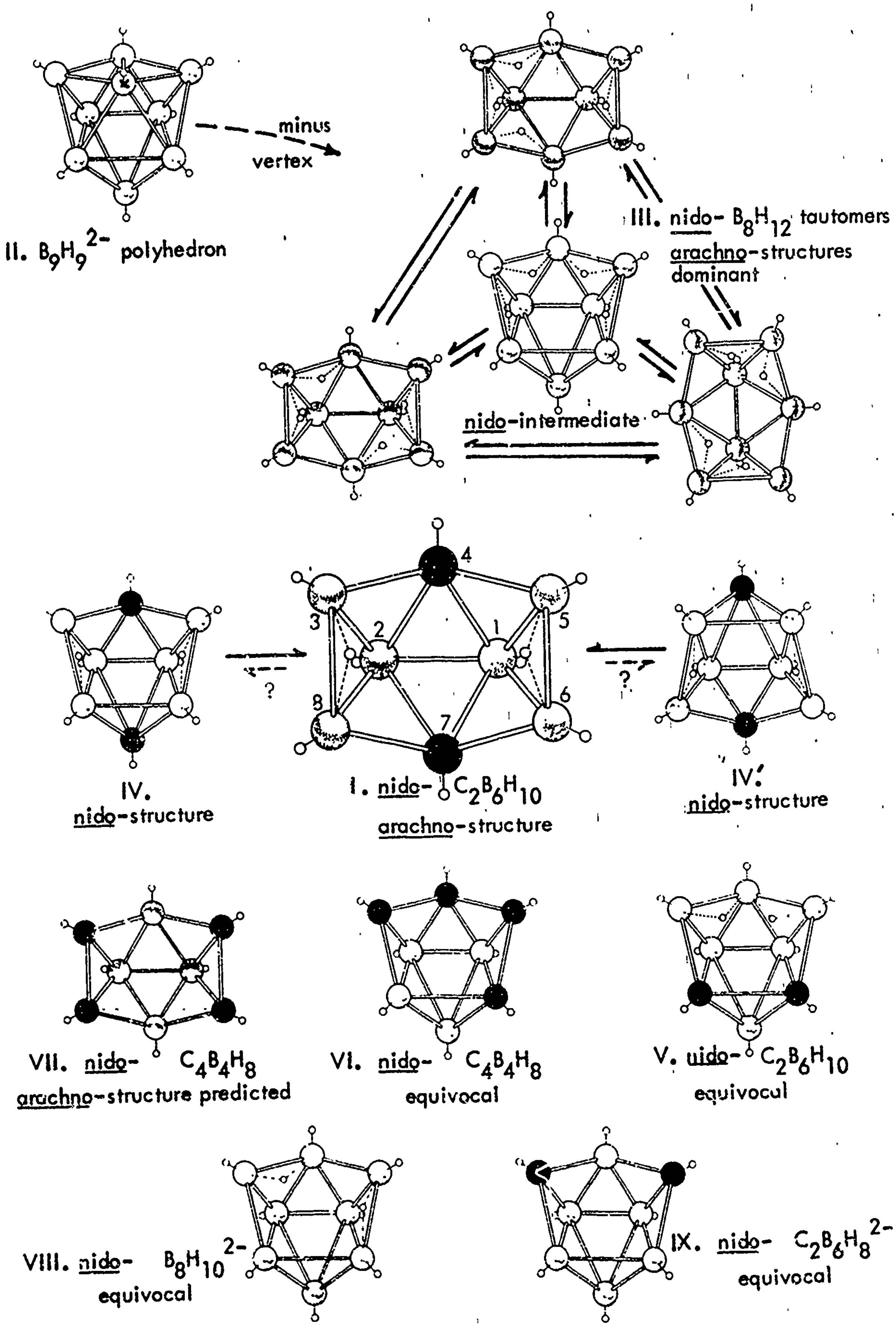
MASS SPECTRUM OF $C_2B_6H_{10}$

Polyisotopic Spectrum

m/e	Intensity
101	0.3
100	13.6
99	22.9
98	58.4
97	100
96	93.4
95	56.0
94	25.8
93	14.2
92	12.1
91	11.3
90	9.9

Monisotopic Spectrum

Ion Species	Intensity
$C_2B_6H_{10}^+$	31.6
$C_2B_6H_9^+$	7.0
$C_2B_6H_8^+$	100
$C_2B_6H_7^+$	73.7
$C_2B_6H_6^+$	16.0
$C_2B_6H_5^+$	9.6
$C_2B_6H_4^+$	3.5
$C_2B_6H_3^+$	9.8
$C_2B_6H_2^+$	6.7
$C_2B_6H_1^+$	6.0



II. $B_9H_9^{2-}$ polyhedron

III. nido- B_8H_{12} tautomers
arachno-structures
dominant

IV.
nido-structure

I. nido- $C_2B_6H_{10}$
arachno-structure

IV'.
nido-structure

VII. nido- $C_4B_4H_8$
arachno-structure predicted

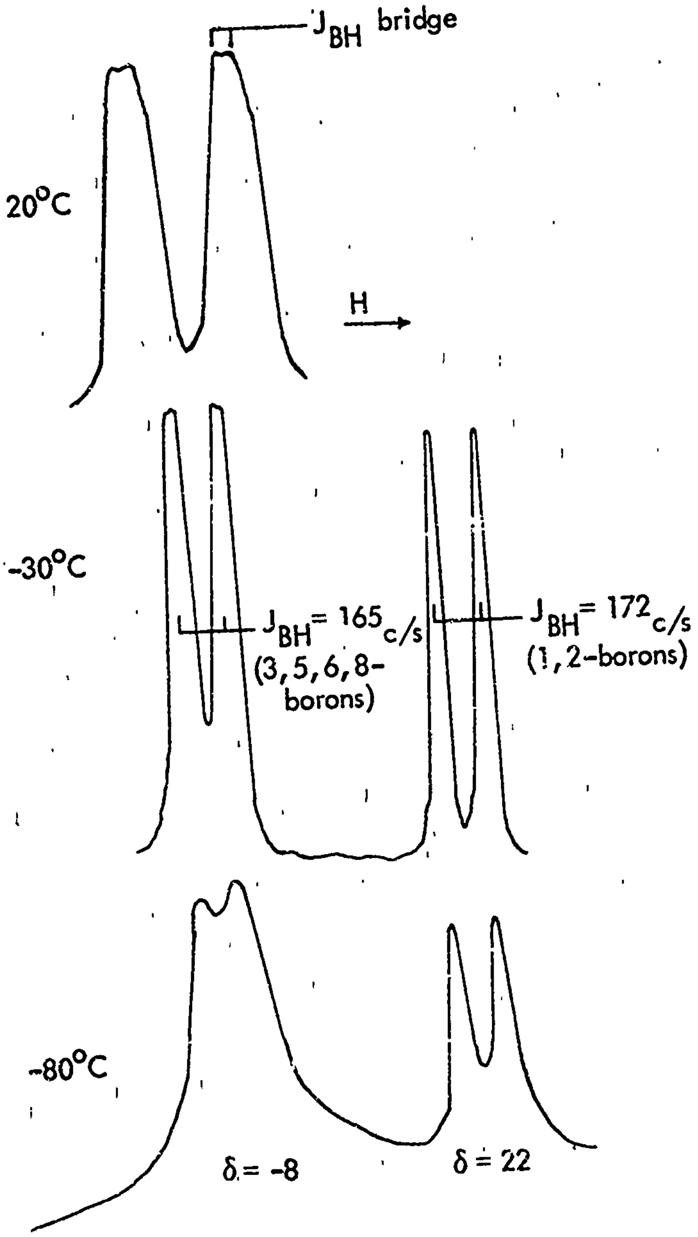
VI. nido- $C_4B_4H_8$
equivocal

V. nido- $C_2B_6H_{10}$
equivocal

VIII. nido- $B_8H_{10}^{2-}$
equivocal

IX. nido- $C_2B_6H_8^{2-}$
equivocal

Figure 1. Eight vertex nido-carboranes of the $C_2B_6H_{10}$-$B_{10}H_{12}$ Family; arachno-configurations dominant.



(These data compare almost exactly with $\delta = -6.8$, $J = 168$ and $\delta = 20.5$, $J = 153$ which must respectively represent the 3,5, 6,8 and 1,2,4,7 sets of borons in the parent B_8H_{12} reported previously)[5]

Figure 2. 32.1 Mc ^{11}BNMR spectrum of 4,7-$C_2B_6H_{10}$ relative to BF_3:etherate.

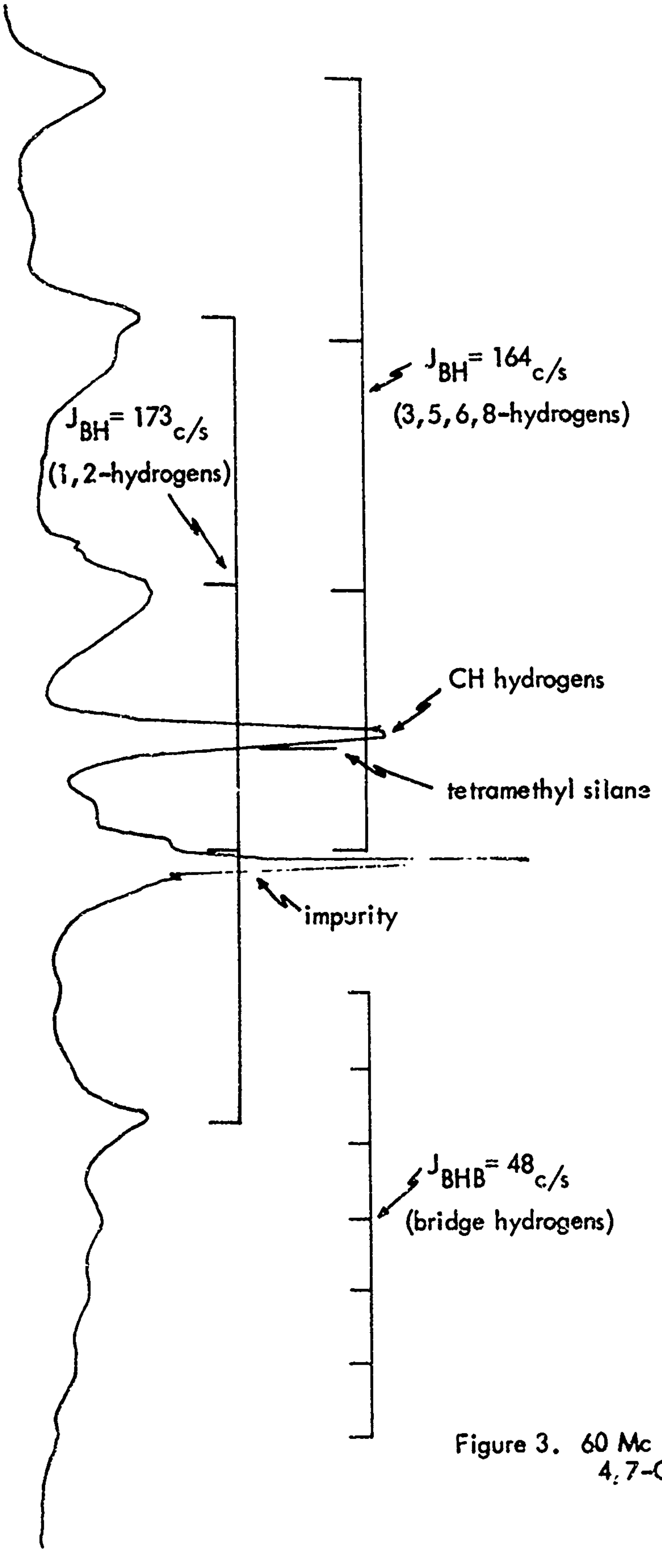


Figure 3. 60 Mc ^{1}H NMR spectrum of $4,7\text{-}C_2B_6H_{10}$.

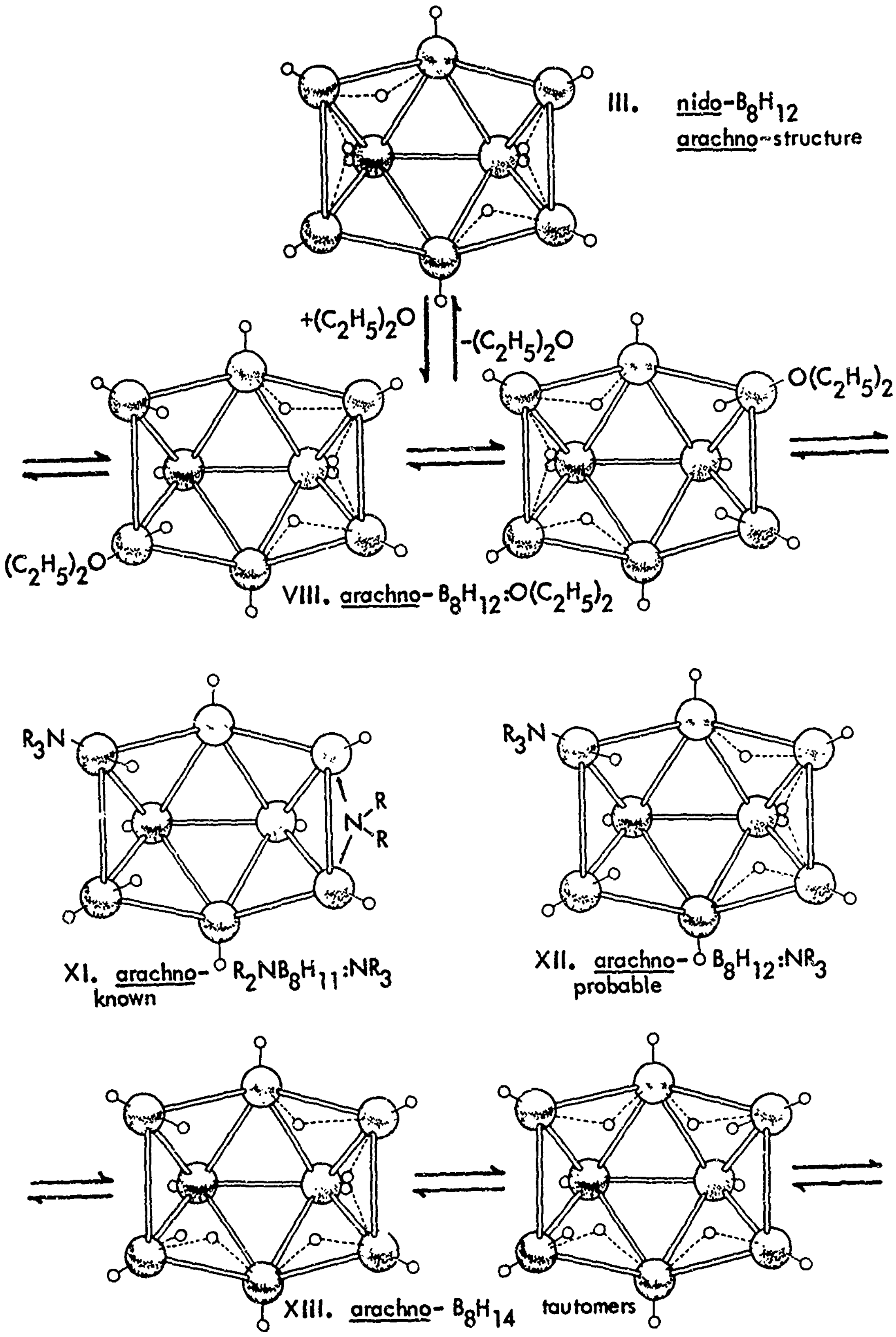


Figure 4. Eight vertex arachno-boranes and arachno-borane Lewis base adducts and their derivatives.

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