COORDINATION NUMBER PATTERN RECOGNITION THEORY OF CARBORANE STRUCTURES*

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I. Introduction

In the early 1950s the structures of the more common boranes were still a matter of debate. Although the hypothesis appeared to be losing favor, there remained strong tendencies to anticipate and interpret borane structures as having *mildly nonconforming hydrocarbon* structures. As a number of boranes were verified as having polyhedral fragment configurations the structural thread to hydrocarbon chemistry became weakened. Subsequently, many other boranes and carboranes were

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discovered, and a seemingly endless array of multifarious structural types had to be considered.

A. VIEWPOINTS ON CARBORANE STRUCTURES

Several schools of thought then arose. Members of one school treated each structure as a separate case, more or less succumbing to the thesis of an almost infinite variety of structural parameters. A second school took the view that although carborane structures were complex in nature, such structures could eventually be categorized or collated by improved theoretical treatments which could be expected to become ever more accurate because of constantly improving computer systems. A third school considered the complexity of carborane structures to be not as severe as had appeared at first view, arguing that when a sufficient number of structures would eventually be determined, the fundamental structural precepts would become decipherable and, consequently, amenable to a simplistic empirical organizational format.

Supporters of each view have made substantial contributions. Advocates of the first school have prepared an almost infinite number of derivatives, whereas subscribers to the second school, in the process of theoretically predicting all possible configurations, generated the correct configuration in a surprisingly large percentage of the cases.

This paper subscribes to the third viewpoint, and is based on an empirical approach that involves coordination number pattern recognition (CNPR). It is a simplistic approach, yet it apparently accommodates most if not all carborane and borane structures. For compounds that are still controversial and for compounds that have not yet been discovered or characterized, the CNPR thesis frequently predicts different structures, or at least fewer candidates, than do any of the theoretical treatments.

The structures, relative stabilities, and relative Lowry-Brønsted acidities of carboranes and boranes as well as related anions, Lewis base adducts, and heteroelement analogs are rationalized primarily on the basis of rudimentary coordination numbers. The principal factors, in decreasing order of importance, are (*a*) the various deltahedra and deltahedral fragments, (*b*) the placement of bridge and endohydrogens, (*c*) the placement of carbon and other heteroelements, and (*d*) the resulting coordination number of boron.

Elucidation of the CNPR theory is based on the presumption *that bridge and endohydrogens (BE hydrogens) when present are of primary structural importance within the carboranes and in related species*. At the very least the theory appears to establish as fact that the influence of BE hydrogens on structure has been vastly underrated.

B. HISTORY OF COORDINATION NUMBER PATTERN RECOGNITION THEORY

In 1971, a note (*164*) was published favoring the hypothesis that the carboranes, boranes, their isoelectronic anions, Lewis base adducts, and heteroatom-substituted analogs should be viewed as constructed about the vertices of either the most spherical series of triangular-faceted polyhedra (deltahedra) found to be characteristic of the dicarba-*closo*-carboranes (Fig. 1) or, with one lone exception, fragments of the series of deltahedra produced by the successive removal of the highest coordinated vertices that sequentially define the nido and arachno classes. This position was in conflict with the then prevalent shibboleth that all nido and arachno compounds [except B_5H_9 (I-N5)] had or would prove to have icosahedral fragment structures.

The 1971 hypothesis (*164*) (throughout this paper referred to as rule 1) may now be expanded by the addition of supplementary rules that deal with the placement of BE hydrogens (rule 2), the placement of carbon and other heteroelements (rule 3), and the consequent coordination situation of boron (rule 4).

Various structures within and among the twenty-five different figures are compared throughout this text. To facilitate reference and cross-reference, all the figures are grouped together in a contrived fashion so that, in Figs. 5 through 19, the last digit or last two digits in the molecular identification numbers not only indicate the figure number but also reflect the number of atoms in the various molecular skeletons. The identifying term I-N5 for B_5H_9, for example, reveals that B_5H_9 is the first structure in Fig. 5; the N denotes that it is a nido species.

Before attempting to outline the supplementary material that expands the original hypothesis, it would appear desirable to establish some degree of credibility by reviewing the present author's research and the many interrelated studies by others.

Included in the 1971 reappraisal (*164*) of carborane structures, and contrary to many alternatively suggested structures pervading the literature at that time, were the following predictions:

1. Nonicosahedral structures should be anticipated for seven- and nine-vertex nido species.
2. The parent B_7H_{11} (I-N7) and B_9H_{13} (I-N9) boranes, which uniquely have unfavorably puckered five-membered open faces (see

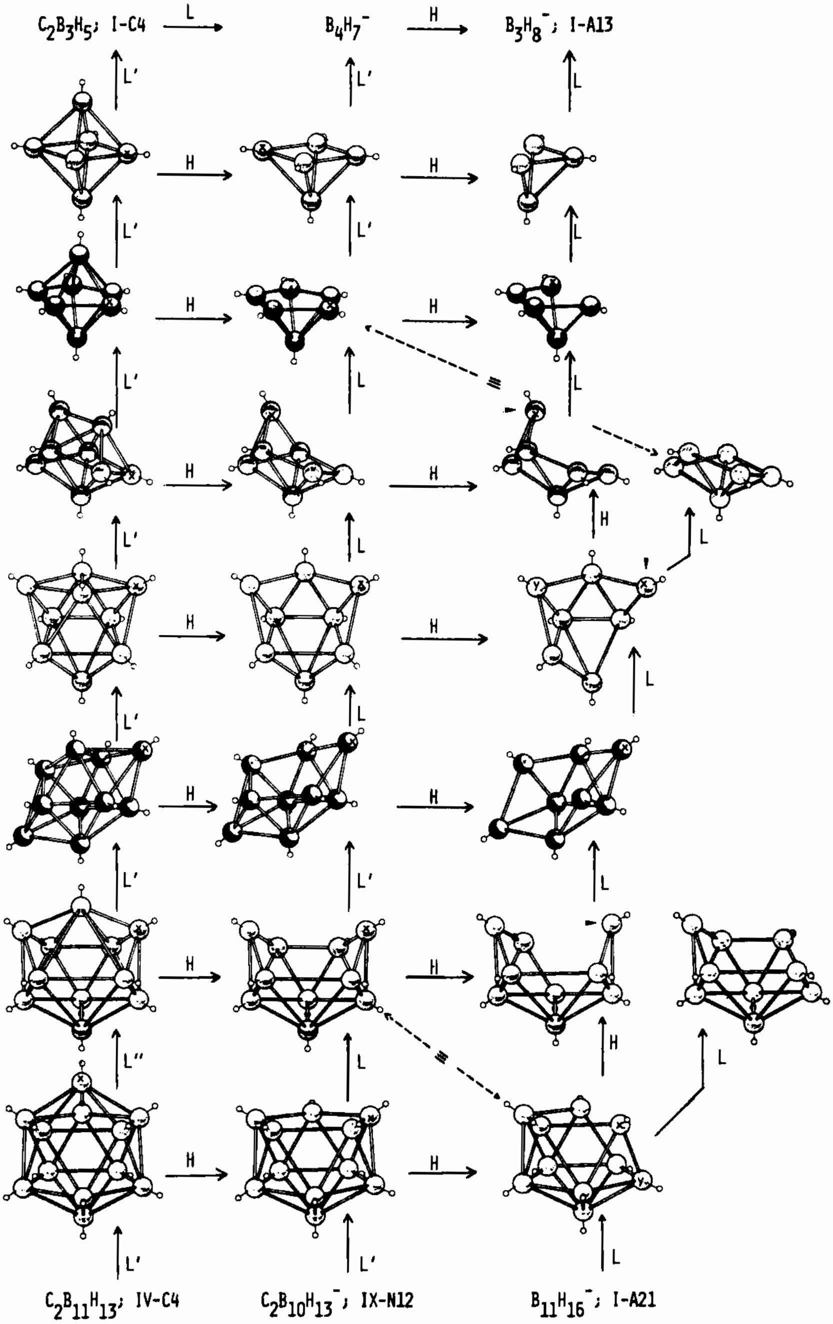


FIG. 1. Deltahedra and deltahedral fragments.

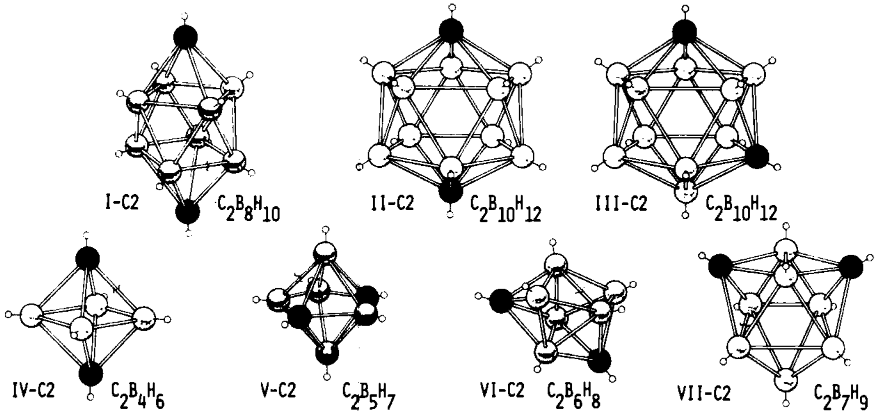


FIG. 2. Stable dicarba-*closo*-carboranes.

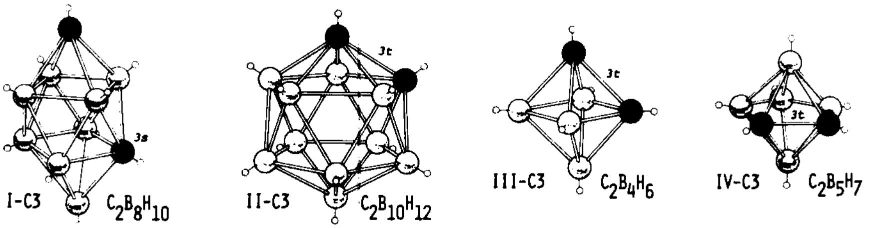


FIG. 3. Rearrangement-prone dicarba-*closo*-carboranes.

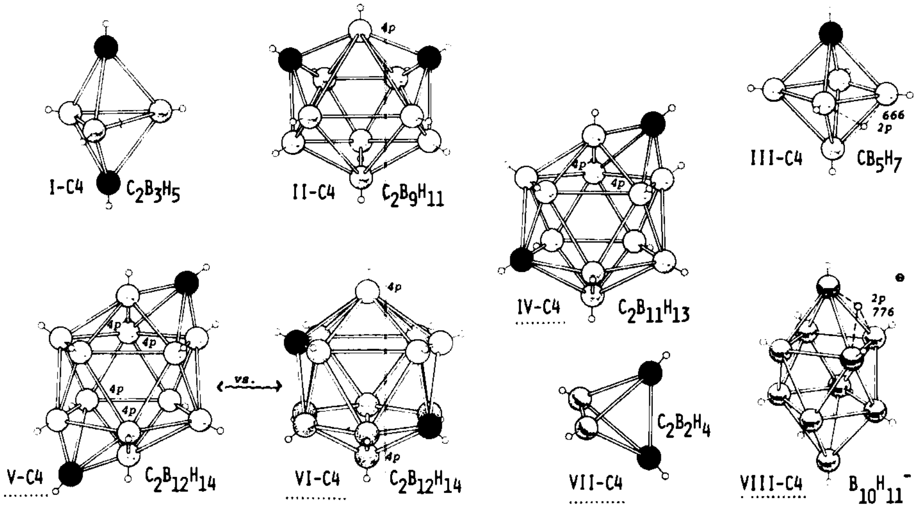


FIG. 4. Unstable and/or unknown *closo*-carboranes.

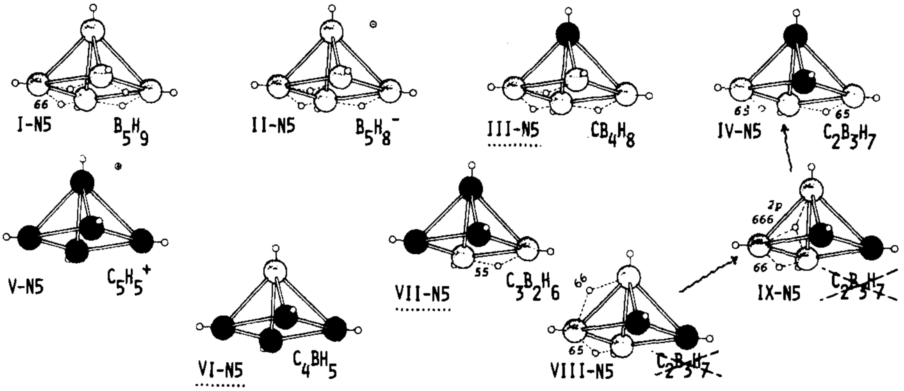


FIG. 5. The B_5H_9 family of *nido*-carboranes.

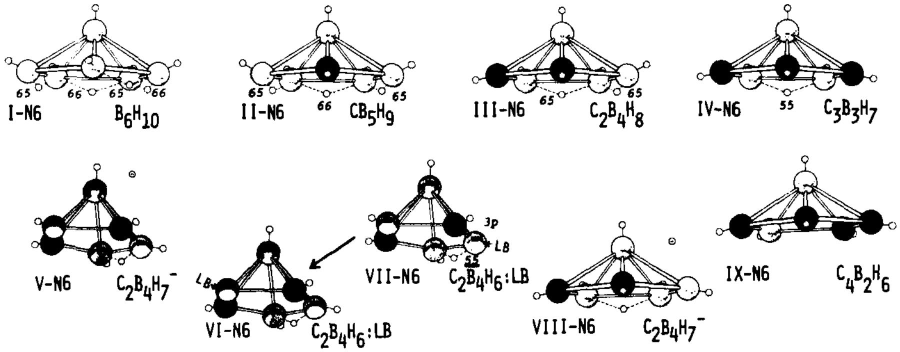


FIG. 6. The B_6H_{10} family of *nido*-carboranes. (LB, Lewis base.)

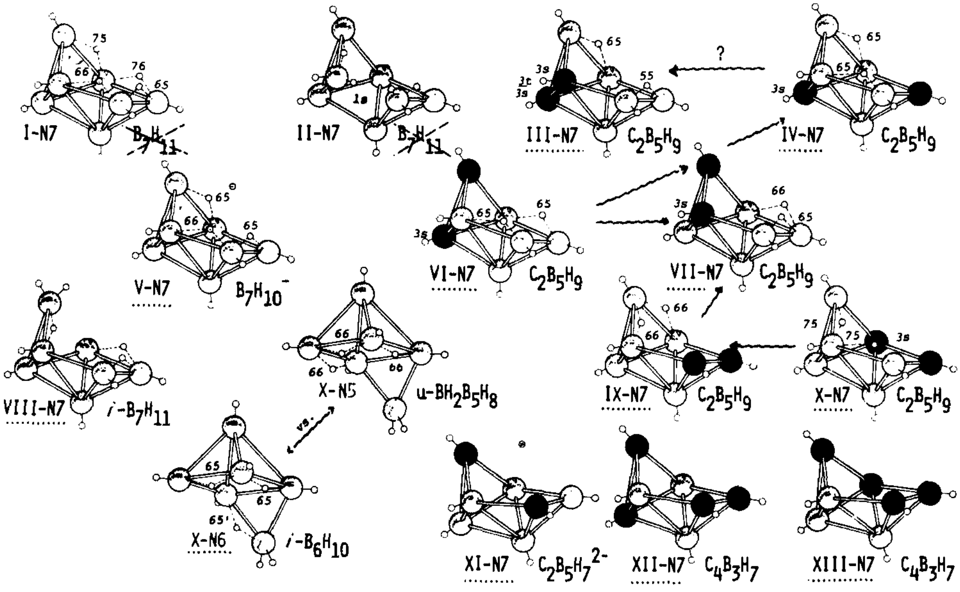


FIG. 7. The $[B_7H_{11}]$ family of *nido*-carboranes.

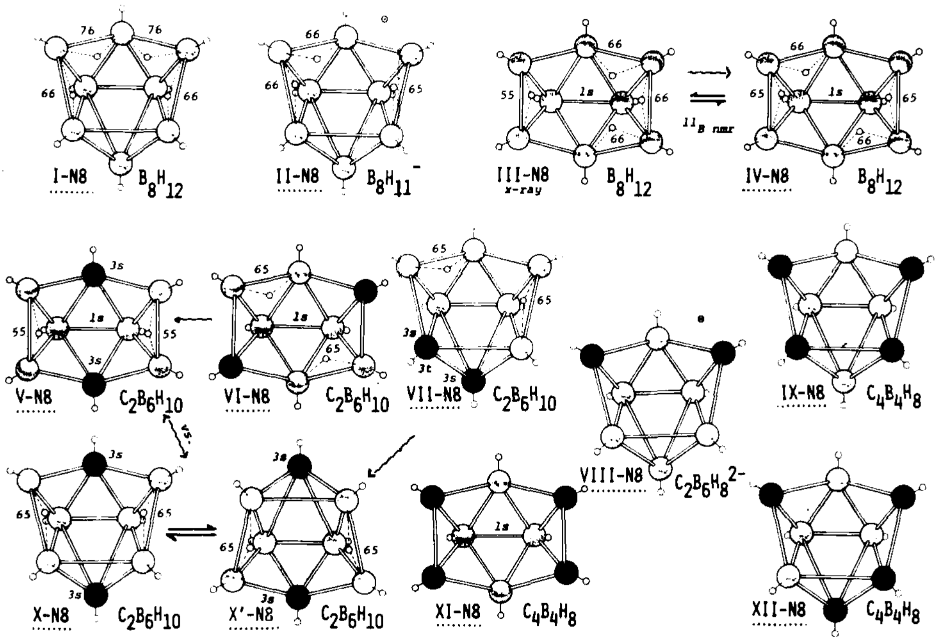


FIG. 8. The B_8H_{12} family of *nido*-carboranes.

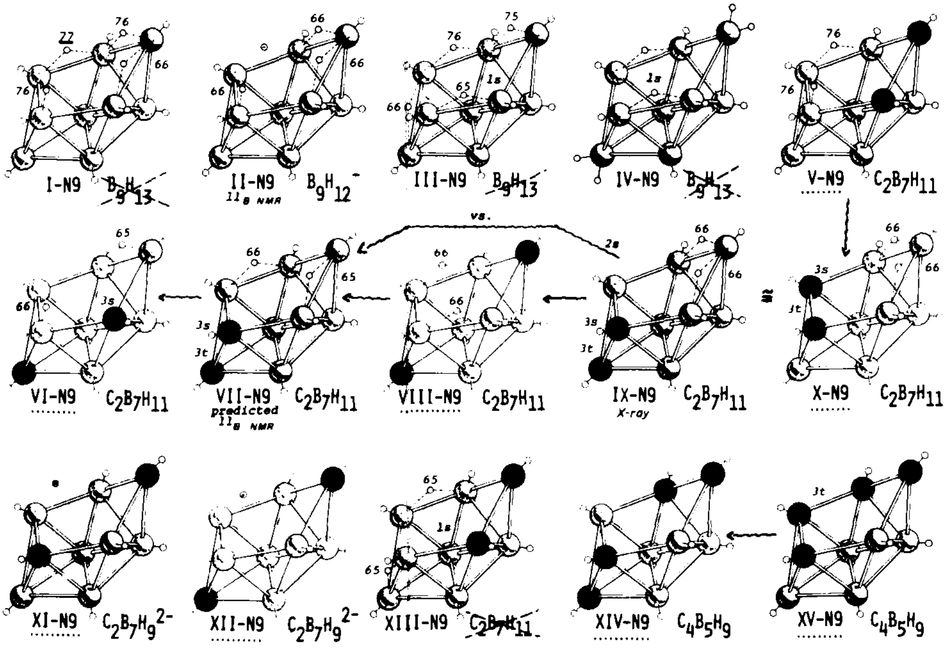


FIG. 9. The $[B_9H_{13}]$ family of *nido*-carboranes.

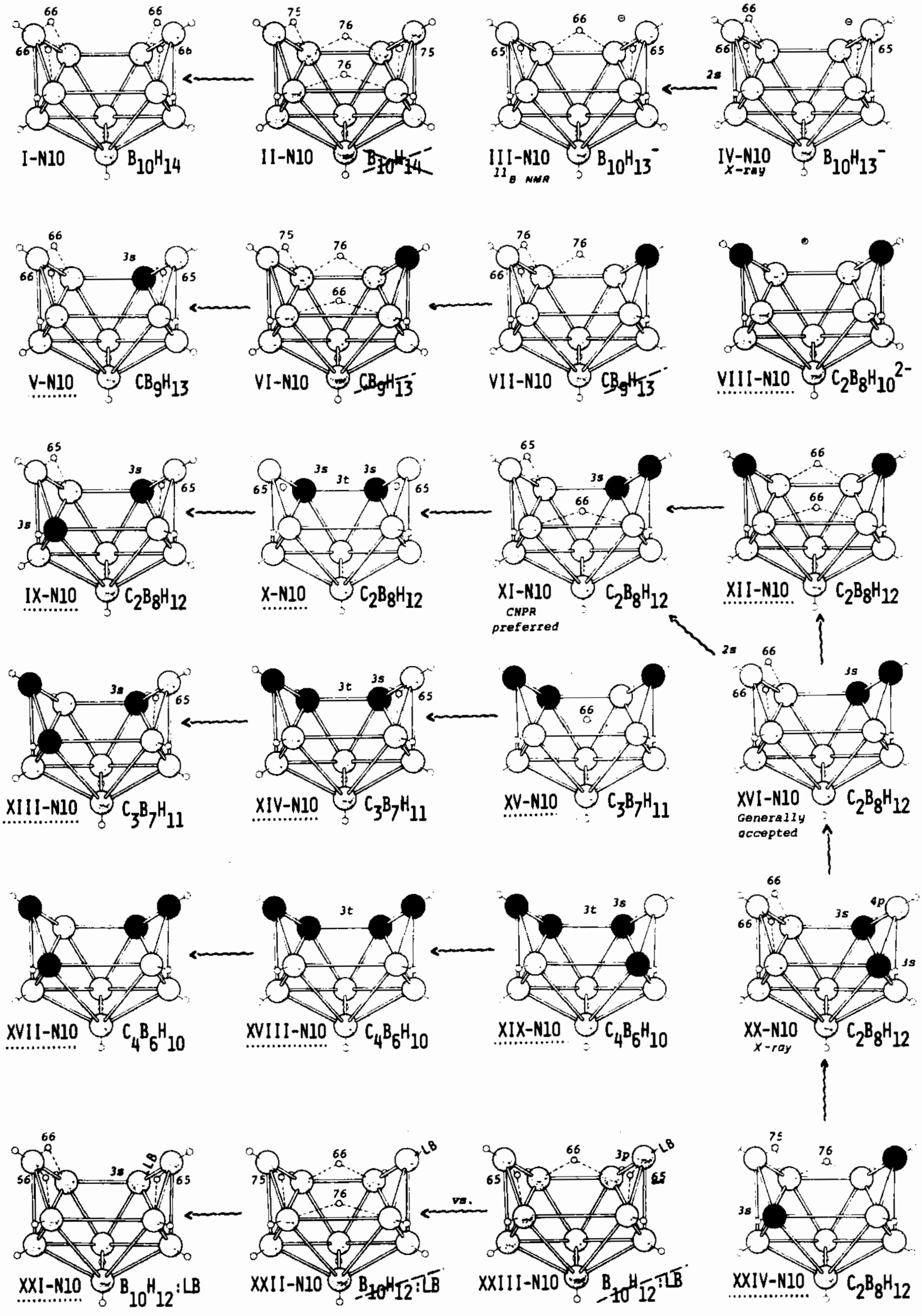


FIG. 10. The $B_{10}H_{14}$ family of *nido*-carboranes. (LB, Lewis base.)

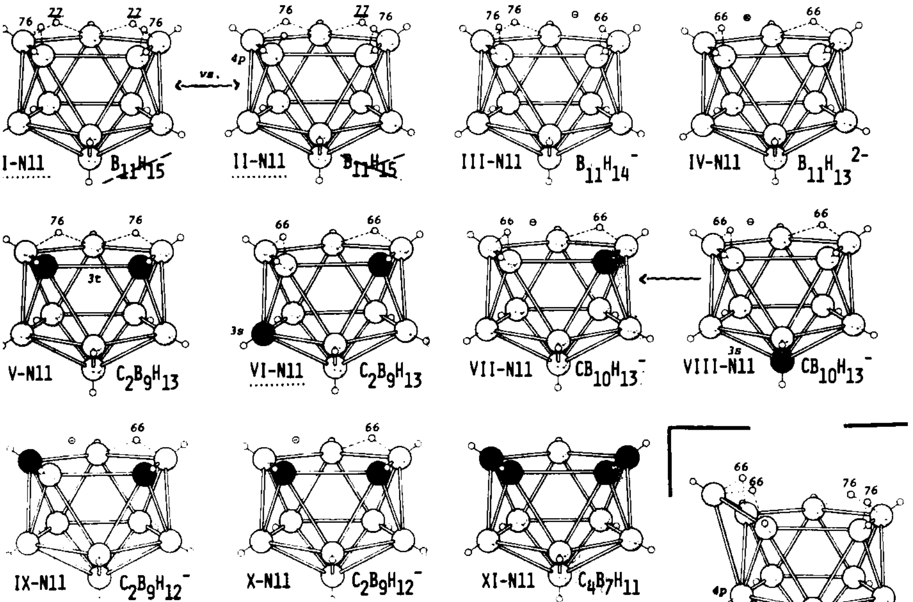


FIG. 11. The [$B_{11}H_{15}$] family of *nido*-carboranes.

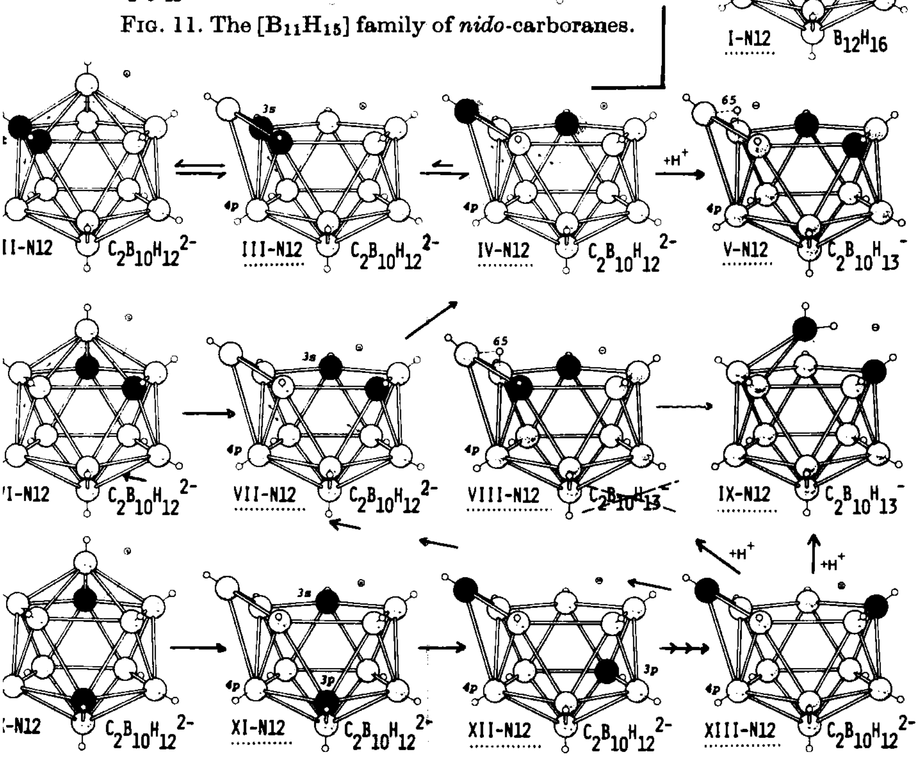


FIG. 12. The [$B_{12}H_{16}$] family of *nido*-carboranes.

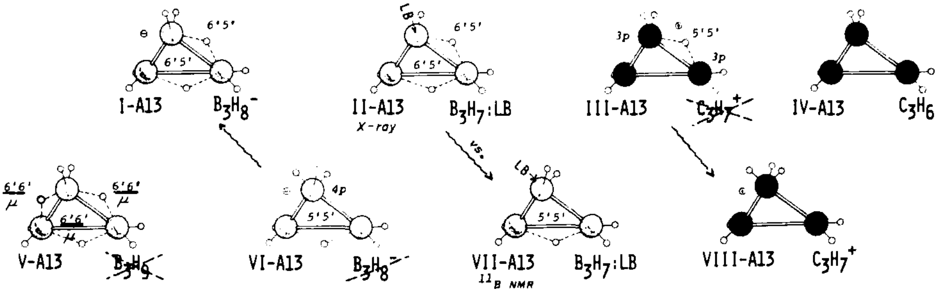


FIG. 13. The [B_3H_9] family of *arachno*-carboranes. (LB, Lewis base.)

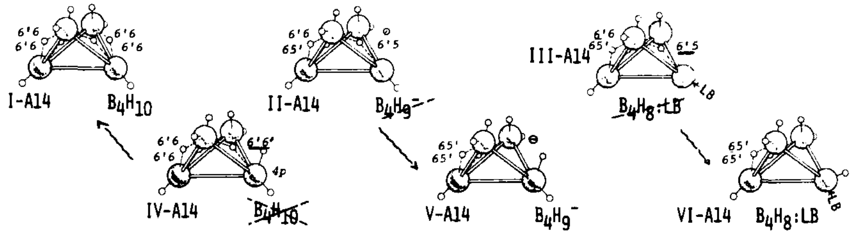


FIG. 14. B_4H_{10} family of *arachno*-carboranes. (LB, Lewis base.)

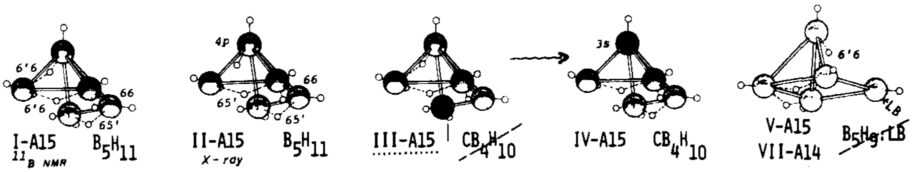


FIG. 15. The B_5H_{11} family of *arachno*-carboranes. (LB, Lewis base.)

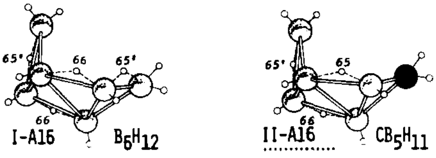


FIG. 16. The B_6H_{12} family of *arachno*-carboranes.

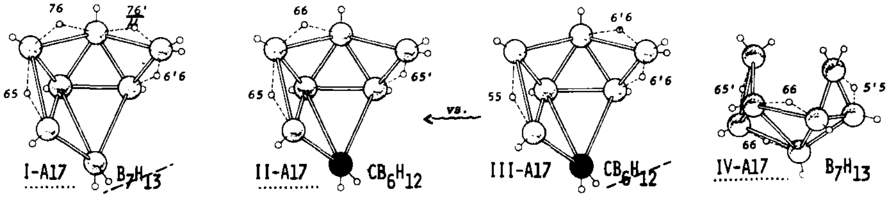


FIG. 17. The [B_7H_{13}] family of *arachno*-carboranes.

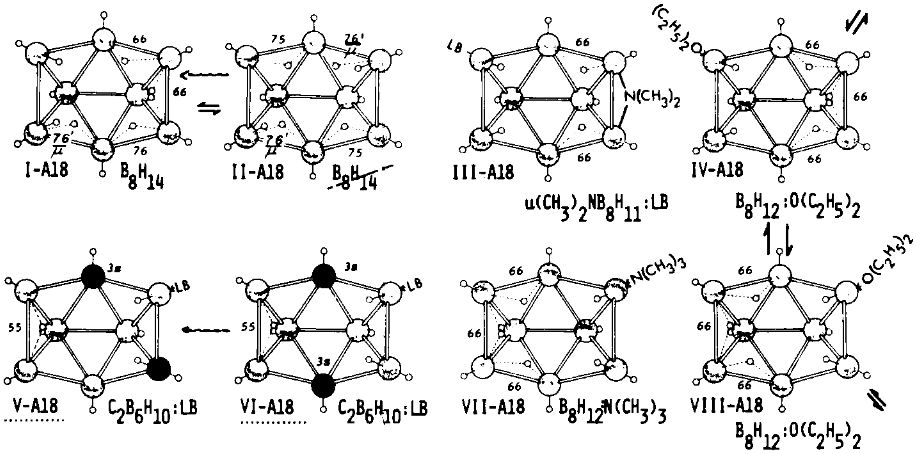


FIG. 18. The B_8H_{14} family of *arachno*-carboranes. (LB, Lewis base.)

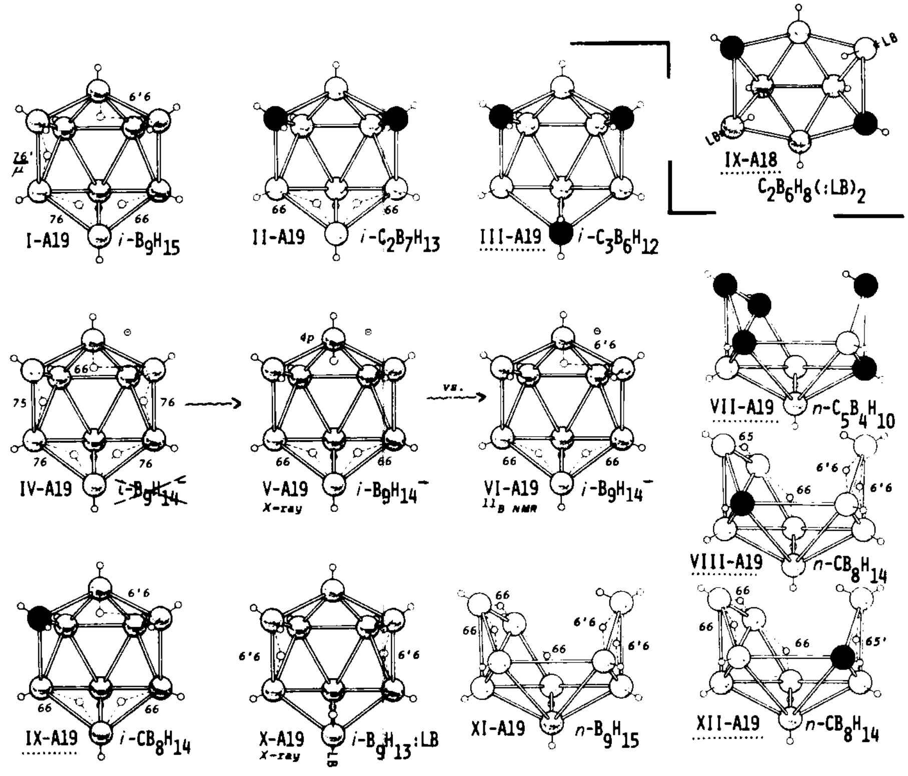
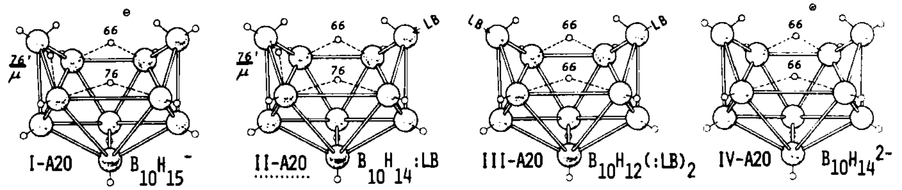
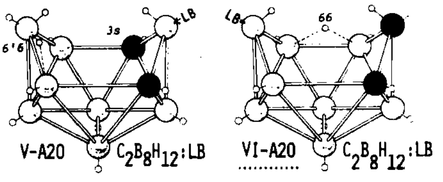


FIG. 19. The B_9H_{15} family of *arachno*-carboranes. (LB, Lewis base.)





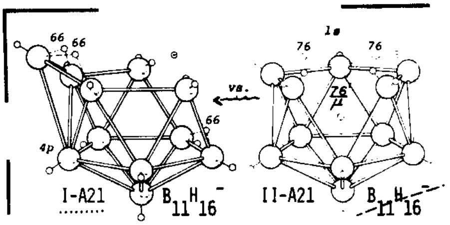


FIG. 20. The $[B_{10}H_{16}]$ family of *arachno*-carboranes. (LB, Lewis base.)

FIG. 21. The $[B_{11}H_{17}]$ family of *arachno*-carboranes.

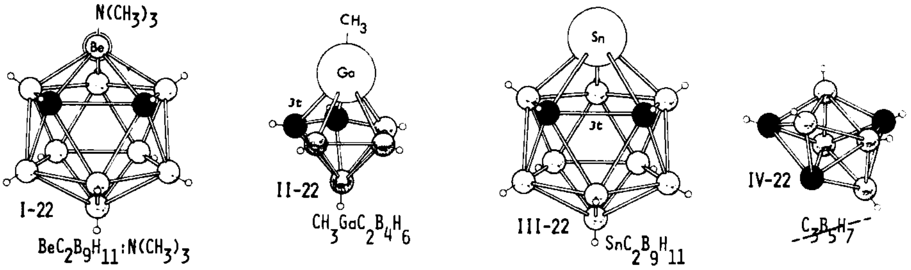


FIG. 22. The BH group-substituted carboranes.

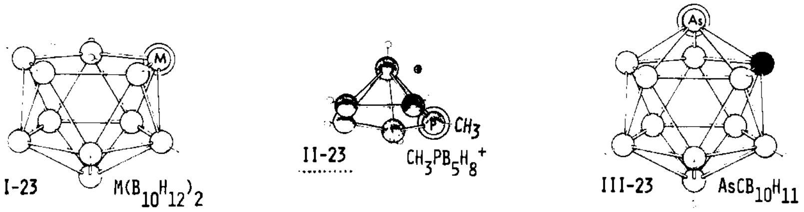


FIG. 23. The CH group-substituted carboranes.

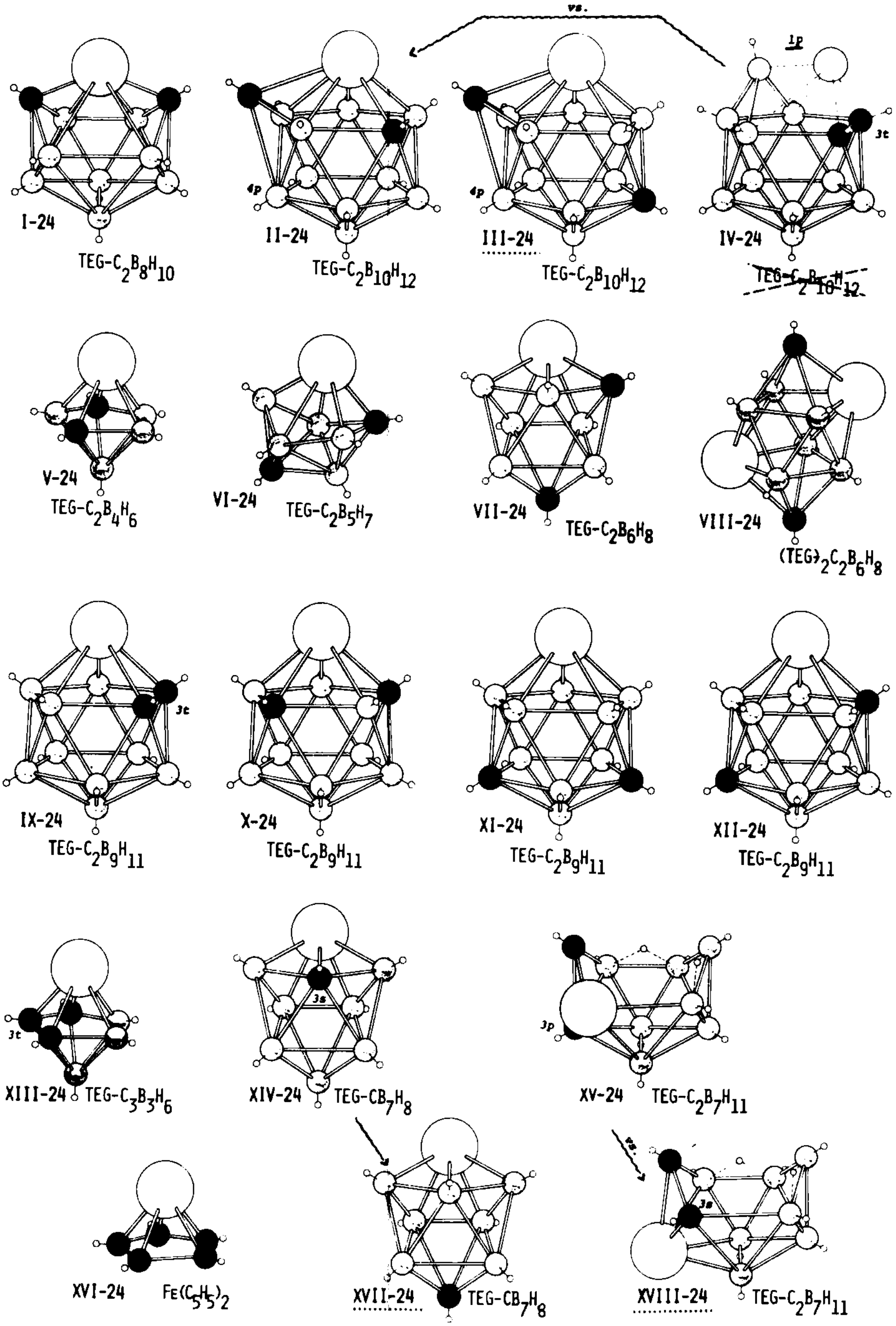


FIG. 24. The transition element group (TEG)-substituted carboranes.

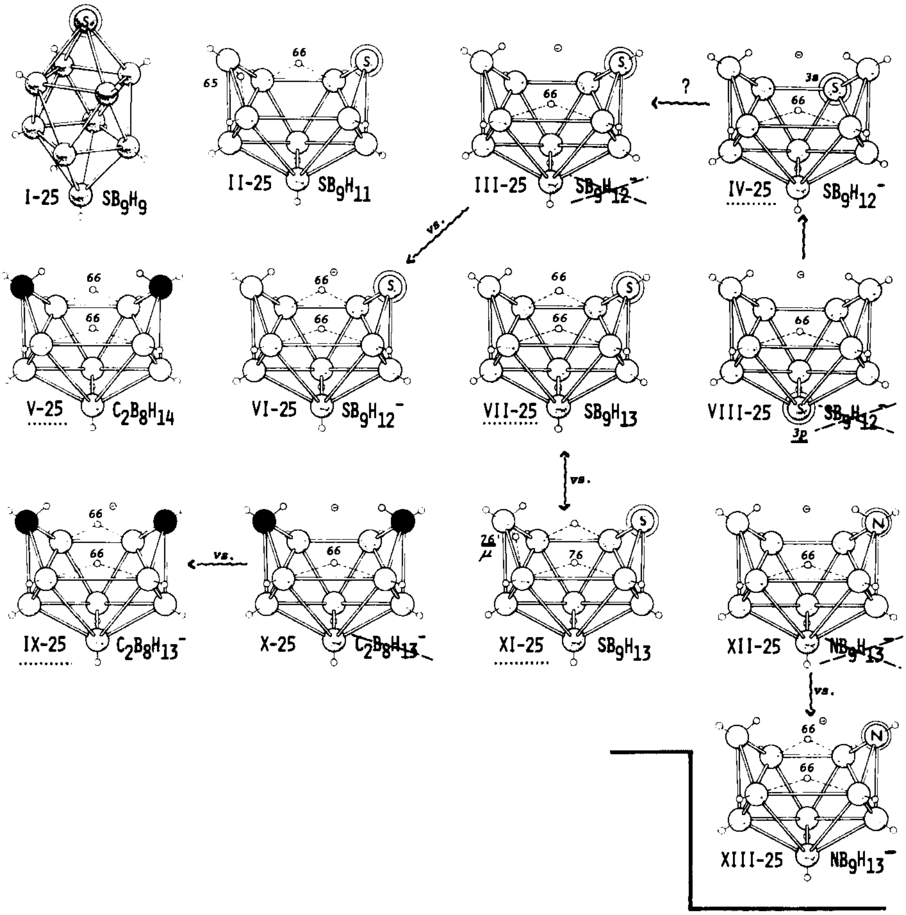


FIG. 25. Comparison of carbathia and carbaaza-substituted carboranes.

Fig. 1) within which to place four bridge hydrogens, may not exist because of steric crowding of the bridge hydrogens. The present author was unable to account for the predilection of the nido eight-vertex B_8H_{12} (III-N8) to assume the more open arachno-structural fragment, at least in the crystal phase (*82*), although to test this exception the isoelectronic $C_2B_6H_{10}$ (V-N8) was isolated.

3. It was also suggested (*164*) on empirical grounds that the "all-carbon" carborane $C_5H_5^+$ (V-N5) would have the skeletal configuration of its parent borane B_5H_9. The following year Hoffman *et al.* (*134*) published their conclusions, based on theoretical grounds, that $C_5H_5^+$ would have a "B_5H_9-like "structure.

Within months, both Wade (*147–152*) and Rudolph *et al.* (*115*, *123*) pointed out that our empirical formula categories for closo, nido, and arachno species (i.e., $C_{0-2}B_nH_{n+2}$ and $C_{0-4}B_nH_{n+4}$ and $C_{0-6}B_nH_{n+6}$) which correlate with the structural rules are similar to Hückel electron-counting rules; i.e., $n+1$, $n+2$, and $n+3$ pairs of skeletal electrons characterize the closo, nido, and arachno classes, respectively (*158*). Others have subsequently paraphrased these same thoughts (*67*, *93*). The antecedent B_nH_{n+4} and B_nH_{n+6} borane categorizations date back through the "systematics" (*110*) of Parry and Edwards (1959) to the original works (*133*) of Stock (1933). The first positively identified *hypho*-borane Lewis base adduct $[(CH)_3P)_2B_5H_9]$ has been structurally characterized by Shore *et al.* (*33a*) and has the structure anticipated by Lipscomb (*82*) for $B_5H_{11}{}^{2-}$. (*Hypho*, from the Greek word meaning "net", is applied to those compounds that are isoelectronic with $C_{0-8}B_nH_{n+8}$ or that have $n+4$ framework electron pairs.) Other hypho species, e.g., B_6H_{10}: $P(CH_3)_3$ (*88a*) and $B_5H_{12}{}^-$ (*117a*), have also been characterized.

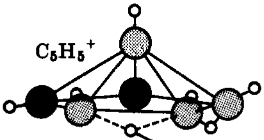
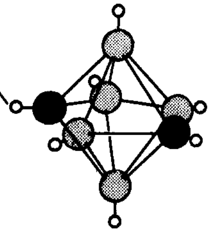
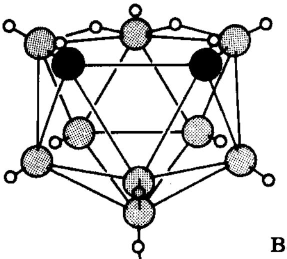
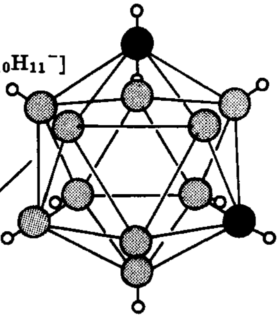
Although many investigators had long been aware that the closo, nido, and arachno (*164*) categories (Table 1) monotonically differed by electron pairs (or their isoelectronic equivalents), it was not generally recognized that electrons associated with endohydrogens could legitimately be considered as skeletal electrons, and, thus, empirical formulas and related isoelectronic relationships (*158*) were focused upon rather than electron count. Both approaches result in the same conclusions and are complementary but the more straightforward skeletal electron counting (*115*, *123*, *147*, *148–152*) seems to be gaining greater acceptance.

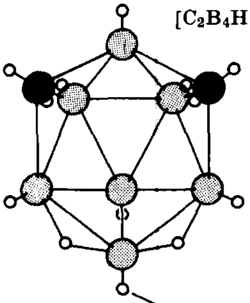
Wade expanded the 1971 hypothesis to incorporate metal hydrocarbon π complexes, electron-rich aromatic ring systems, and aspects of transition metal cluster compounds [a parallel that had previously been noted by Corbett (*19*) for cationic bismuth clusters]. Rudolph and Pretzer chose to emphasize the redox nature of the closo, nido, and arachno interconversions within a given size framework, and based the attendant opening of the deltahedron after reduction (diagonally downward from left to right in Fig. 1) on first- and second-order Jahn–Teller distortions (*115*, *123*). Rudolph and Pretzer have also successfully utilized the author's approach to predict the most stable configuration of SB_9H_9 (I-25) (*115*) and other thiaboranes.

A number of studies published since 1971 confirm several of the initial predictions. Two groups at Indiana University [Siedle *et al.* (*128*) and Streib *et al.* (*61*)] have revealed that the nine-vertex nido structures $B_9H_{12}{}^-$ (II-N9) and the isoelectronic *C*,*C*-dimethyl derivative of $C_2B_7H_{11}$ (IX-N9) *do have nonicosahedral fragment structures* (see Figs. 1 and 9;

TABLE I

CORRELATION CARBORANES BY EMPIRICAL FORMULA

	closo-			*nido-*				
	Carboranes		Boranes	Carboranes				Boranes
4								
5	$C_2B_3H_5$			$C_5H_5^+$			$B_5H_8^-$	B_5H_9
6	$C_2B_4H_6$ $[C_1B_5H_6^-]$ $B_6H_6^{2-}$	$C_1B_5H_7$		$C_4B_2H_6$	$C_3B_3H_7$ $C_2B_4H_7^-$	$C_2B_4H_8$	$C_1B_5H_9$	B_6H_{10}
7	$C_2B_5H_7$ $B_7H_7^{2-}$							
8	$C_2B_6H_8$ $B_8H_8^{2-}$							B_8H_{12}
9	$C_2B_7H_9$ $B_9H_9^{2-}$						$B_9H_{12}^-$	
10	$C_2B_8H_{10}$ $C_1B_9H_{10}^-$ $B_{10}H_{10}^{2-}$	$[B_{10}H_{11}^-]$		$[C_4B_6H_{10}]$	$[C_3B_7H_{11}]$	$C_2B_8H_{12}$ $B_{10}H_{12}^{2-}$	$B_{10}H_{13}^-$	$B_{10}H_{14}$
11	$C_2B_9H_{11}$ $C_1B_{10}H_{11}^-$ $B_{11}H_{11}^{2-}$			$C_2B_9H_{11}^{2-}$ $C_1B_{10}H_{11}^{3-}$	$C_2B_9H_{12}^-$	$C_2B_9H_{13}$ $C_1B_{10}H_{13}^-$ $B_{11}H_{13}^{2-}$	$B_{11}H_{14}^-$	$B_{11}H_{15}$
12	$C_2B_{10}H_{12}$ $C_1B_{11}H_{12}^-$ $B_{12}H_{12}^{2-}$							
	C_2	C_1	B_nH_{n+2}	C_4	C_3	C_2	C_1	B_nH_{n+}
	$C_{0-2}\ B_nH_{n+2}$			$C_{0-4}B_nH_{n+4}$				
	$n + 1$ skeletal electron pairs			$n + 2$ skeletal electron pairs				

			arachno-				
		Carboranes			$B_3H_8^-$	Boranes	
						B_4H_{10}	4
						B_5H_{11}	5
C_6H_6				$[C_2B_4H_{10}]$		B_6H_{12}	6
$C_7H_7^+$							7
						B_8H_{14}	8
				$C_2B_7H_{13}$	$B_9H_{14}^-$	B_9H_{15}	9
				$B_{10}H_{14}^{2-}$	$B_{10}H_{15}^-$		10
							11
							12
C_6	C_5	C_4	C_3	C_2	C_1	B_nH_{n+6}	

$C_{0-6}B_nH_{n+6}$

$n + 3$ skeletal
electron pairs

see also prediction 1 in the preceding). Moreover, Masamune (*89*) recently demonstrated that $C_5H_5^+$ (V-N5) apparently has the B_5H_9 (I-N5) configuration (see prediction 3). In addition, Hogeveen and Kwant (*59*) have isolated a permethyl derivative of $C_6H_6^{2+}$ that is isoelectronic and isostructural with $C_4B_2H_6$ (IX-N6) and B_6H_{10} (I-N6) and which reinforces to an even greater extent the structural parallels in borane, carborane, and carbonium ion chemistries.

An investigation of $C_2B_6H_{10}$ (V-N8; isoelectronic with B_8H_{12} and possessing even fewer bridge hydrogens) did not resolve the dilemma regarding eight-vertex nido compounds. The possible assumption of an arachno eight vertex structure by *nido*-$C_2B_6H_{10}$ suggests that something may be uniquely different about the nido eight-vertex polyhedral fragment.

If the bonding in B_8H_{12} and in $C_2B_6H_{10}$ is described in terms of 2- and 3-center bonds, then four 3-center bonds should reside within the skeletal framework and, in spite of the more open arachno structure, the required four 3-center bonds are successfully accommodated, at least in the crystalline phase. The possibility that the true nido structures (I-N8 for B_8H_{12} and X-N8 for $C_2B_6H_{10}$) may exist in the fluid phases is under investigation.

There have been complementary reports by several investigators encouraging an expansion of the original deltahedron (*164*) deltahedral fragment postulate. Among these reports are the revelations by Siedle *et al.* (*129*) and Schaeffer *et al.* (*132*) of the two different tautomeric structures (involving bridge hydrogen placement) of $B_{10}H_{13}^-$ in the fluid phase (III-N10; unencumbered tautomer) as opposed to the crystal phase (IV-N10; encumbered tautomer) where crystal packing forces evidently play a role (*78*, *144*). These results herald the demise of a second belief that bridge and endohydrogens occupy the same locations in both the unencumbered fluid phase as well as in the encumbered crystalline phase. Other kinds of bridge hydrogens are also known to be distorted by the crystal environment, e.g., F_2H^- (*156*).

Shore's investigations (*65*) of the structure of $B_4H_9^-$ (V-A14), to be compared with Parry and Paine's studies (*39*, *109*) of B_3H_7:LB (VII-A13), as a function of temperature, coupled with Onak's *et al.* study (*88*, *106*) of Lewis base migration in the isomerization of *nido*-$C_2B_4H_6$:$N(CH_3)_3$ (i.e., VI-N6 is produced from VII-N6) expose certain patterns that relate to the predictable equivalence in some cases and to the predictable nonequivalence in other cases of a Lewis base (:LB) and/or a hydride (H^-) in such structures.

Beaudet *et al.* (*3*) have demonstrated that the bridge hydrogen of CB_5H_7 (III-C4) is on the cage (i.e., located over a triangular facet) and is thus involved in a 4-center bond.

Hawthorne and his associates (*60*, *155*) have reassuringly shown that the previous suggestions (*160*) are correct regarding bridge hydrogen placement in $CB_{10}H_{13}^-$ (VIII-N11) and the two isomers of $C_2B_9H_{12}^-$ (IX- and X-N11), as well as the anticipated (*159*) placement of the carbon in *closo*-$CB_{10}H_{11}^-$ [this in spite of a previously published alternative structure (*62*)].

The following sections expand on the deltahedron–deltahedral fragment hypothesis (structural rule 1), and in the order of decreasing importance add three additional rules, one involving the placement of BE hydrogens (rule 2), next the placement of the various heteroelements (with emphasis on carbon) (rule 3) (*172*), and finally the structural accommodations of boron, including the influences of endohydrogens (rule 4). All are shown to have their roots *firmly and simply* embedded in CNPR considerations.

What is thus offered is in effect a "back of the envelope" systematization of carborane–borane structures of predictive and teaching utility.

II. Structural Rules

A. REAPPRAISAL OF DELTAHEDRON–DELTAHEDRAL FRAGMENT HYPOTHESIS (RULE 1)

In its abridged form the deltahedron–deltahedral fragment hypothesis (*164*) itemizes the various closo deltahedra in the left vertical column in Fig. 1. Deletion of one highest coordination vertex site from each of the closo deltahedra produces the nido deltahedral fragments displayed in the middle vertical column of Fig. 1. Removal of one additional highest coordination vertex from the nido-deltahedral fragments (necessarily adjacent to the open faces in the case of boranes and carboranes) produces the skeletal configurations characteristic of the arachno series in the right vertical column in Fig. 1.

There is an exception: in addition to the expected normal arachno nine-vertex fragment characteristic of *n*-B_9H_{15} (XI-A19) (*78*, *130*), there is a fragment generated by the removal of a low coordination vertex which is reflected in the structures of both *i*-B_9H_{15} (I-A19) (*21*) and its isoelectronic analog *i*-$C_2B_7H_{13}$ (II-A19) (*136*).

The nido ten-vertex and arachno ten-vertex deltahedral fragments are coincidently the same. *Such ten-vertex nido and arachno species are not isoelectronic*, although they are frequently misjudged as being isoelectronic, and a number of investigators have assigned incorrect structures based on comparison of ^{11}B NMR spectra of compounds that were mistakenly thought to be isoelectronic.

Figure 1 was initially generated by removing high-coordination vertices horizontally (*164*) (shown as process H in Fig. 1), but the consequences of removing low-coordination vertices (shown as process L, L′, or L″ in Fig. 1) are also illuminating. (The primes reflect the number of "bonds" necessarily reintroduced following the vertex removal.)

If one vertex and its attendant bonds are removed from a ball-and-stick model of the closo twelve-vertex icosahedron and two bonds are subsequently inserted into the open face, the eleven-vertex deltahedron results. If from each resulting smaller deltahedron any one of the lowest-coordination vertices, and its attendant bonds, are monotonically removed and one bond is inserted, the next smaller deltahedron results in all cases, from the icosahedron to the trigonal bipyramid. It was the exact reverse of this primitive ball-and-stick degradation concept (process L) which allowed the correct bisdisphenoid (*154*) structure for $C_2B_6H_8$ (VI-C2) to be anticipated (*172*) prior to its production.

A similar appraisal of the vertical middle row in Fig. 1 (the nido fragments) shows that basic process L also applies in all cases excepting that, in following low coordination vertex removal, bonds must be inserted in the ten- to nine-vertex and six- to five-vertex cases (process L′).

The vertical relationships between adjacent arachno fragments are illustrated in the right vertical row in Fig. 1. The ten- to nine-vertex arachno transformation (via process L) yields the unpredicted (by process H) *i*-nine-vertex arachno fragment instead of the *n*-nine-vertex arachno fragment. And, to convert the hypothetical seven-vertex arachno fragment to the known six-vertex arachno fragment, removal of a high-coordination edge vertex is required; removal of the low-coordination vertex produces an arachno fragment that is identical to the six-vertex nido fragment. The alternative six-vertex arachno fragment is very unlikely to be observed for any *arachno*-carborane.

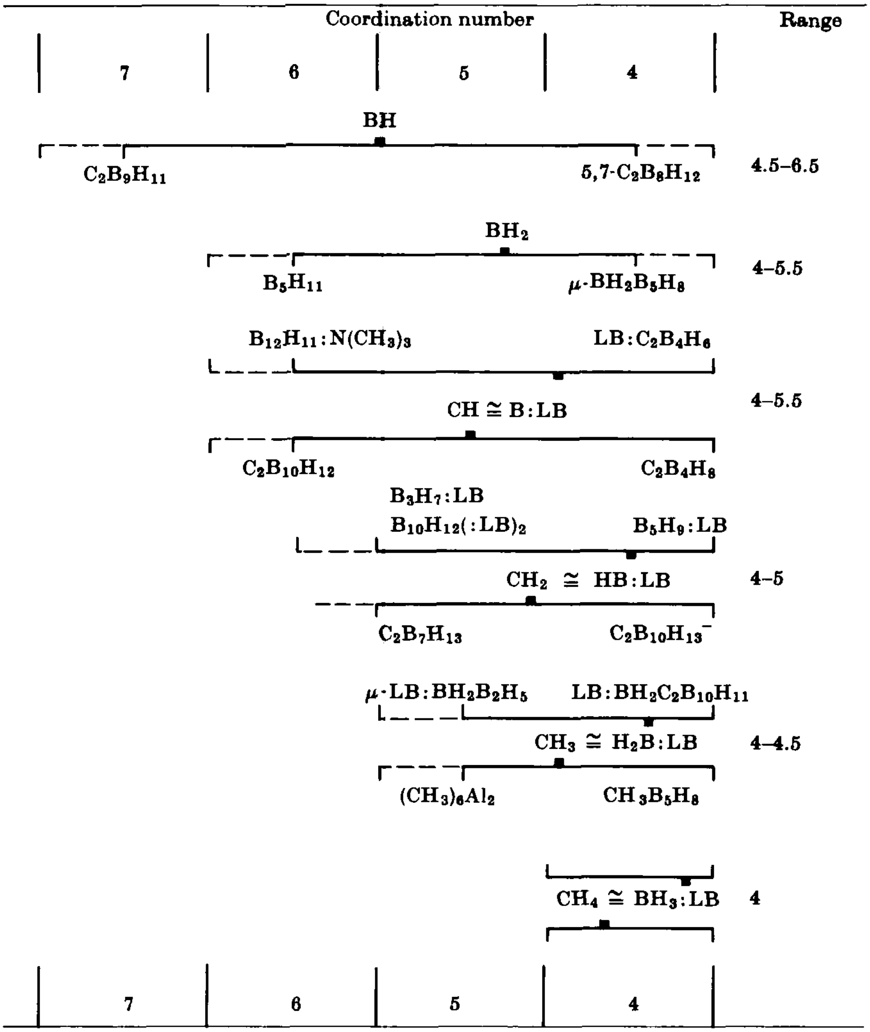
B. STRUCTURAL PREFERENCES OF VARIOUS MOIETIES: PRELUDE TO THE EXPOSITION OF RULES 2, 3, AND 4

In order to recognize the patterns that pervade carborane chemistry, it is instructive to conduct a "molecular census," to ascertain where and in what coordination-number environments the various groups, e.g., BH, BH_2, CH, CH_2, CH_3, and Lewis base equivalents (B:LB, BH:LB, and BH_2:LB, where LB = Lewis base) are most frequently found. Table II itemizes the various groups; obvious trends may be observed and examples of the extreme cases are given.

The term *coordination number* of a given atom is used herein to define the total number of other atoms with which the given atom is

TABLE II

COORDINATION NUMBER RANGE OF VARIOUS GROUPS



associated. The borons in B_2H_6 are, therefore, each five-coordinate as they are associated with two terminal hydrogens, two bridge hydrogens, and one other boron.

Note that BH groups are most amenable to varying coordination-number environments (5-7), whereas BH_2 groups (less electrons to delocalize) are less amenable to high-coordination number environments

TABLE III

VIOLATIONS OF VARIOUS RULES

Rule 1	Rule 2	Rule 3	Rule 4
Primary Skeletal configurations that are not deltahedra or deltahedral fragments displayed in Fig. 1	Primary Bridge hydrogens associated with more than two borons (i.e., XXX-bridge hydrogens)	Primary Carbons found in sites two coordination numbers higher than otherwise present, or adjacent to bridge hydrogens	↑ ? Primary BH groups found in seven- or four-coordinate sites, or BH_2 groups found in six-coordinate sites, or BH_3 groups found in five-coordinate sites ↓ ?
↑ ? Secondary Skeletal configurations displayed in Fig. 1 but in incorrect series ↓ ?	Secondary Two-coordinate bridge hydrogens occupying higher-coordination sites when lower-coordination alternatives are present, or the presence of 77-, 76-, and 6′6-bridge hydrogens	Secondary Carbons found in sites one coordination number higher than otherwise present	
		Tertiary Carbons adjacent when both are over four-coordinate	

TABLE IV

EXAMPLES OF VARIOUS RULE VIOLATIONS

Rule 1	Rule 2	Rule 3	Rule 4
1p None or maybe $C_2B_{10}H_{13}^-$ (IX-N12)	2p CB_5H_7 (III-C4) $B_{10}H_{11}^-$ (VIII-C4)		
↑ ?		3p None or maybe [$C_2B_4H_6$:LB[a](VII-N6)] TEG-$C_2B_7H_{11}$(XV-24)	↑ ?
1s B_8H_{12} (III-N8) $C_2B_6H_{10}$ (V-N8) B_7H_{13} (IV-A17)	2s $B_{10}H_{13}^-$ (IV-N10) $C_2B_7H_{11}$ (IX-N9) $C_2B_8H_{12}$ (XI,XVI,XX-N10) $B_{11}H_{15}$ (I-N11) *i*-B_9H_{15} (I-A19) B_7H_{13} (I-A17)	3s 1,6-$C_2B_8H_{10}$ (I-C3) $CB_{10}H_{13}^-$ (VIII-N11)	4p $C_2B_9H_{11}$ (II-C4) $B_{11}H_{15}$ (II-N11) $B_3H_8^-$ (VI-A13)
↓ ?		3t 1,2-$C_2B_4H_6$ (III-C3) 1,2-$C_2B_{10}H_{12}$ (II-C3)	↓ ?

[a] LB, Lewis base.

and probably more amenable to lower-coordination number environments. Carbon is less adaptable than boron, thus B:LB groups (isoelectronic with CH groups) are found to be only slightly more tractable than carbon to the various structural environments (in one or two cases B:LB groups have been found adjacent to bridge hydrogens).

The CH_2 groups are less tractable than CH groups. The seeming predilection of carbon to be found in a five-coordinate CH_2 environment with the *arachno*-carboranes rather than in a five-coordinate CH environment, e.g., $C_2B_7H_{13}$ (II-A19) is thought to be the result of the endohydrogen's preference rather than that of the carbon. (Both are "electron-sufficient" and prefer to engage in localized bonding if possible.) However, in the absence of the endohydrogen requirements, a five-coordinate CH group would be preferred over a five-coordinate CH_2 group.

The definition here of electron-deficient as compared to electron-sufficient is keyed to the number of electrons lacking in the boron species as compared to the equivalent carbon species; thus, B_4H_{10} is four electrons deficient compared to a neutral C_4H_{10}. In almost all cases the number of electrons deficient coincides exactly with the number of simplistic 3-center bonds [the $s + t$ of Lipscomb's styx terminology (*82*)] necessary to describe the structure. Again, B_5H_9 (I-N5) requires five 3-center bonds whereas $B_5H_8^-$ (II-N5) would require four 3-center bonds and $C_5H_5^+$ (V-N5) require one 3-center bond. All three species have one skeletal 3-center BBB or CCC bond, whereas the other 3-center bonds are expressed as 3-center bridge hydrogens. An alternative and more general definition of electron deficiency has been used by Wade (*147a*).

Rule 1 and the additional rules 2, 3, and 4 are displayed (in abridged form) in Tables III and IV (during the exposition of the rules, the reader may benefit by referring to these tables).

C. BRIDGE AND ENDOHYDROGEN CONSIDERATIONS (RULE 2)

The recognition of the significance of the BE hydrogens in carborane structures and function is the feature that made possible the formulation of CNPR theory. The relative importance of bridge hydrogen placement as opposed to carbon placement was settled in favor of the bridge hydrogens when Grimes deduced the structure of $C_2B_3H_7$ to be IV-N5 (*32*, *33*, *45*, *168*) instead of VIII-N5 (*162*). Both bridge hydrogens and carbons favor sites of lowest-coordination number; however, in the case of $C_2B_3H_7$ the bridge hydrogen preempted the lowest-coordination environment at the expense of carbon (*168*).

Were the isoelectronic anion (i.e., $C_2B_3H_6^-$) to be prepared, the most stable configuration should have adjacent basal carbons to accommodate the basal bridge hydrogen as well as the carbon. Either cis or trans basal carbons should be anticipated in the isoelectronic dianion ($C_2B_3H_5^{2-}$) which would have no bridge hydrogens. Rudolphs's Extended Hückel Molecular Orbital calculations would favor cis basal carbons in the latter case.

Although not realized until recently, in all probability a bridge hydrogen, if forced to assume a position upon the cage [as is the case with CB_5H_7 (III-C4)], would locate over a triangular face (*3*) and would hence be associated with three borons via a 4-center bond as illustrated in IX-N5.

In contrast to the convention of counting the adjacent atoms alone when assigning rudimentary coordination numbers to either the carbon or boron, ***the bridge hydrogen convention applied here counts the coordination numbers of the two (or rarely three) borons with which the bridge hydrogen is associated.*** For example, all of the two-coordinate bridge hydrogens in $B_{10}H_{14}$ (I-N10) are referred to as 66-bridge hydrogens since all of the borons associated with the bridge hydrogens are six-coordinate (including the bridge hydrogens in the count). The four bridge hydrogens in B_6H_{10} (I-N6) are similarly labeled as two 66-bridge hydrogens and two 65-bridge hydrogens. Since, as can be seen from Table II, BH_2 groups are less amenable to higher coordination situations, a prime is added when one (or both) of the borons associated with a bridge hydrogen is a BH_2 group; thus the bridge hydrogens in B_2H_6 are 5′5′-bridge hydrogens whereas those in B_4H_{10} (I-A14) are 6′6-bridge hydrogens.

Bridge hydrogens prefer the lowest-coordination sites, avoiding if possible borons whose coordination numbers are 7 or 6′. There are patterns beyond the scope of the present manuscript suggesting that a bridge hydrogen associated with a seven-coordinate BH group is less content (i.e., more labile or more acidic) than with a 6′-coordinate BH_2 group. Nevertheless, all known compounds with $\underline{77}$-, $\underline{76'}$- and $\underline{6'6'}$-bridge hydrogens are unstable and are considered as equivalently undesirable throughout this manuscript.

Disregarding steric congestion, it is much more than coincidence that the "stable" *nido*-boranes B_5H_9 (I-N5), B_6H_{10} (I-N6), and $B_{10}H_{14}$ (I-N10) incorporate only 66- and 65-bridge hydrogens, whereas the unobserved structures for the unstable *nido*-boranes B_7H_{11} (I-N7), B_8H_{12} (I-N8), and B_9H_{13} (I-N9) would contain 76-, 75-; two 76-; and two 76- and $\underline{77}$-bridge hydrogens, respectively.

The latter two species, B_8H_{12} (I-N8) and B_9H_{13} (I-N9), may be considered to "eliminate" the overly coordinated 7X-bridge hydrogens by either opening into the arachno configuration B_8H_{12} (*121*) (III- and IV-N8) which incorporates 66-bridge hydrogens or by the elimination of one proton from B_9H_{13} to form $B_9H_{12}^-$ (II-N9) which also incorporates only 66-bridge hydrogens!

Bridge hydrogens are thought to seek sites between lowest coordinated borons because of the bridge hydrogen's attraction to the most "electron available" environment. Noted throughout the text are the many cases where electronegative anions (more electrons available) stabilize more highly coordinated bridge hydrogens than are stabilized on isoelectronic neutral molecules. When heteroatoms furnish the requisite skeletal electrons within neutral molecules, the heteroatoms become positively charged. Such positively charged locations are shunned by bridge hydrogens and, thus, we find no bridge hydrogens neighboring carbon, sulfur or nitrogen (or rarely borons associated with Lewis bases as they are isoelectronic with carbon). Indeed, as discussed in Section III, E, even terminal hydrogens avoid sulfur and nitrogen. The positive charge centered about the heteroatom that repels adjacent bridge hydrogens, might also affect more remote locations. Such heteroatoms could possibly account for bridge hydrogens in selected compounds being found in slightly higher coordinated locations more distant from the heteroatom when lower coordinated locations were available closer to the heteroatom (see XI-N10 v. XVI-N10 and VII-N9 v. IX-N9). This possible longer range effect of heteroatoms is currently neglected but should be considered seriously in future investigations.

It is safe to assume that any XXX-bridge hydrogen on a cage, e.g., as in CB_5H_7 (III-C4) (*3*), and associated with three 6-coördinate borons (a 666-bridge hydrogen) would be in a very undesirable situation. Similarly, three coordinate bridge hydrogens in the hypothetical closo species ($B_{12}H_{14}$) and ($B_{10}H_{12}$) [or $B_{10}H_{11}^-$ (VIII-C4)] would be $\underline{777}$- and $\underline{776}$-bridge hydrogens, respectively. This could account for the fact that such species have heretofore only been known as $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ ions (*95*) and that the related acids ($(H_3O^+)_2B_nH_n^{2-}$) are very strong acids.

Under rule 2, the instability of a three-coordinate bridge hydrogen occupying any cage site (e.g., $\underline{666}$) is pointed out as a primary violation, whereas a two-coordinate bridge hydrogen occupying a higher coordination site when a lower coordination site is available is defined as a secondary violation. The various violations are noted about the molecules within the figures by the symbols (2s), etc. For example, (2s) denotes that the molecule depicted involves a secondary violation of rule 2 (see Tables III and IV).

Compound B_3H_9 (V-A13), which would have three very undesirable 6′6′-bridge hydrogens, has never been isolated, and both $B_{11}H_{15}$ [I-N11 (*28*) with perhaps two 77-bridge hydrogens] and $B_{10}H_{15}^-$ [I-A20 (*122*) with a 76′-bridge hydrogen] are known to be very unstable. The closely related B_2H_6 (two 5′5′-bridge hydrogens) and $B_{11}H_{14}^-$ [III-N11 (*1*), two 76-bridge hydrogens] are more stable, and as would be expected, the related $B_{11}H_{13}^{2-}$ (IV-N11) with two compliant 66-bridge hydrogens is much more stable (*34*).

In those instances where packing forces in the crystalline state evidently induce the bridge hydrogens in molecules, such as $B_{10}H_{13}^-$ [(III-N10 (*129*) vs. IV-N10 (*132*)] and probably $C_2B_7H_{11}$ [IX-N9 vs. VII-N9 (*61*)], to assume less desirable (i.e., higher-coordination) situations, to date, only conflicts between structurally preferable XX-bridge hydrogens (where X = 6 or 5 rather than 6′ or 7) appear to be involved.

The 6′6-bridge hydrogens in B_4H_{10} (I-A14) are biased toward the more desirable 6-boron and away from the 6′-boron (*82*).

D. Carbon and Other Heteroelement Atom Considerations (Rule 3)

From the discovery of the first carboranes it was noted that the carbons were in the apex positions in $C_2B_3H_5$ (I-C4) (*40, 90, 126, 175*) but were in the equatorial positions in $C_2B_5H_7$ (V-C2) (*104*); i.e., *they were in the lowest-coordination positions possible in each case.* Furthermore, it was observed that the carbons, if one or both were over four-coordinate, tended to be separate or to separate at least in the *closo*-carboranes; e.g., the 1,6-$C_2B_4H_6$ (IV-C2) (*40, 90, 126, 175*) isomer was produced by heating the 1,2-$C_2B_4H_6$ (III-C3) isomer (*100*). These CNPR considerations made it possible to publish the correct (and only the correct) carbon position isomers for both 2,4-$C_2B_5H_7$ (V-C2) (*4, 5, 104*) and 1,7-$C_2B_6H_8$ (VI-C2) (*172*), in spite of ambiguous ^{11}B NMR data.

Upon closer scrutiny it becomes apparent that these considerations revealed by carbon's predilections are general and apply to the other heteroelement carboranes as well.

It is now recognized that the predisposition of most, if not all, two-coordinate bridge hydrogens are more important (rule 2s) than the positioning of carbon when carbon's coordination number choices differ by 1 (rule 3s). Isomers in violation of the foregoing rules are known (i.e., carbons are found in ideal situations at the expense of the ideal placement of the bridge hydrogens), but in such cases the ideal carbon isomers are less stable than their ideal bridge hydrogen analogs. A carbon would probably be least likely to be found two coordination numbers higher (i.e., in a six- rather than a four-coordinate site) to accommodate the desire of bridge hydrogens to migrate to slightly lower-coordination sites. When such a situation is eventually encountered it will be defined as a primary violation of rule 3 (see Tables III and IV and XI-N12 and XII-N12).

The bridge hydrogen vs. carbon competition for low-coordination sites is further complicated by the capability of the bridge hydrogens to migrate (*157*) into ideal sites even under ambient conditions if not in the encumbered crystalline phase. Carbon migration (in the absence of seven-coordinate borons), in contrast, usually requires elevated temperatures for migration to other sites; e.g., the 1,2-$C_2B_4H_6$ (III-C3) rearrangement (*100*) into 1,6-$C_2B_4H_6$ (IV-C2). Furthermore, under pyrolytic conditions, carbons never (to date) migrate in such a fashion as to become adjacent (violating rule 3t) in the final products although such migration might be necessary to attain the more stable, i.e., ideal bridge hydrogen structure.

Thus, although thermodynamically best isomers may be predicted (with bridge hydrogens in optimal positions and carbons in next best positions), frequently the chemical precursors kinetically dictate that the carbons will be placed in the wrong positions for producing the best isomer. In these cases the bridge hydrogens (mobile at ambient conditions) migrate to the best positions available, whereas the carbons are immobile unless elevated temperatures are involved. It is these same mobile bridge hydrogens which, on occasion, succumb to crystal packing forces and assume different bridge hydrogen configurations (*129*, *132*) in the encumbered crystal phase (e.g., $B_{10}H_{13}^-$ has structure IV-N10 rather than III-N10) and, on occasion, even become endohydrogens rather than bridge hydrogens [e.g., $B_9H_{14}^-$, (V-A19) (*43*); B_9H_{13}:LB (X-A19) (*153*); and B_5H_{11} (II-A15) (*79*)] to accommodate such crystal packing forces.

E. Boron Considerations (Rule 4)

As perceived in Table II, BH groups are found to have the greatest coordination number range (5–7) while BH_2 groups have a more restricted range (4–6) probably due to the localizing effect of the additional endo-terminal hydrogen that militates against the high-coordination predispositions of the electron-deficient boron.

In order to catalog specific undesirable architectural loci under as few rule violations as possible, "content or malcontent" endohydrogens have been included (when not adjacent to bridge hydrogens) under rule 4.

For cataloging purposes the borons are considered as speciously more important than the endohydrogens when comparing content or malcontent BH_2 groups (rule 4). By contrast, if bridge hydrogens neighbor a BH_2 group such architectural conditions are considered as content or malcontent bridge hydrogens (rule 2) rather than content or malcontent BH_2 groups under rule 4.

Although avoiding organizational difficulties, this approach generates a separate problem because, as will become apparent, there is a continuum of BE hydrogens, some pure bridge (covered under rule 2) and some pure endo (covered under rule 4), with several specific examples defined as somewhere in between pure bridge and pure endo [e.g., B_5H_{11} (I- and II-A15)].

Seven-coordinate BH groups [e.g., $C_2B_9H_{11}$ (II-C4) (*2*, *135*, *145*)] as well as six-coordinate BH_2 groups not associated with bridge hydrogens [e.g., B_5H_{11} (II-A15)] are both associated with structural instability; both cases are considered to be violations of rule 4p. In the former case it may be assumed that it is malcontent boron that finds itself in an overly coordinated situation, whereas in the latter case it is understood to be a combination of malcontent boron and malcontent endohydrogen.

When bridge hydrogens are involved as neighbors of seven-coordinate BH or six-coordinate BH_2 groups, then the architectural indiscretions are considered to be secondary violations of rule 2 rather than involving rule 4. In this contrived fashion, tabulating a single undesirable locus as violating more than one rule is avoided.

The suggested rules having been itemized in the previous sections, a chemical rationalization of their origins follows, after which the various types and families of boranes and carboranes are discussed in detail.

F. PRIMARY, SECONDARY, AND TERTIARY EXPRESSIONS OF RULES 1, 2, 3, AND 4

Had the patterns become apparent in the numerical order of importance rather than in the order rule 3(1956), 1(1970), 2(1971), and 4(1972), their organization would have been simpler.

The rules in overall decreasing order of importance essentially state that the ideal structures for carboranes will be based on most spherical deltahedra (rule 1); the BE hydrogens will tend to be placed in the lowest possible coordination environments (rule 2); when elements to the right of boron in the periodic table are incorporated into the deltahedron or deltahedral fragment, they will tend to preempt low-coordination sites (e.g., carbon) or, if electron-deficient, high coordination sites (rule 3); and, lastly, boron will eschew seven-coordinate BH or six-coordinate

BH_2 environments (rule 4). In actual fact, however, selected compounds either comply marginally or violate the rules to varying degrees. In the sense that these few exceptions define the limits of the rules, it is useful to break the rules down into subsets of varying importance. Thus a primary violation of rule three (3p) may be a more serious offense than a secondary violation of the more important rule 2 (2s).

The rules are displayed in abridged form in Tables III and IV. They are deliberately described in the negative sense; i.e., rather than describing or listing the innumerable architectural features which do conform to the various rules, Tables III and IV emphasize the limited numbers of architectural features that are considered to be either on the borderline of acceptability or verging on violating the various rules.

In an oversimplified manner, the relative importance of the various rules (i.e., 1, skeletal; 2, bridge hydrogen; 3, carbon; 4 boron) have been rationalized on CNPR considerations as outlined in the following.

It has long been recognized that when there are fewer electrons available for bonding, more bonds are produced, e.g., in the series B_2H_6, C_2H_6, and N_2H_6 (i.e., $2NH_3$), 12, 14, and 16 electrons are available, respectively, for bonding (although in inverse order 9, 7, and 6 bonds are observed). It follows that the select series of most spherical deltahedra, in accordance with rule 1, maximizes the geometrical opportunities for multiple bonding and that the most electron-deficient *closo*-boranes ($B_nH_n^{2-}$) and *closo*-carboranes ($C_{0-2}B_nH_{n+2}$) will be found in the closed, most spherical, deltahedral configurations.

In countering the icosahedronism belief (*164*) the series of most spherical deltahedra (left-hand column in Fig. 1) may have been overemphasized. The most spherical deltahedra were correctly preferred because of coordination number smoothing; i.e., it follows that the eight-vertex bisdisphenoid incorporating five- and six-coordinate vertices is preferable when all of the atoms are boron ($B_8H_8^{2-}$) or boron and carbon [$C_2B_6H_8$ (VI-C2)] as opposed to the hexagonal bipyramid (seven- and five-coordinate vertices) and perhaps the bicapped trigonal antiprism (*154*) (four- and six-coordinate vertices). The ideal four-coordinate sites for carbon in the latter deltahedron involve overly acute angles as in $C_2B_3H_5$ (I-C4).

As the initial paper (*164*) was concerned only with boron and carbon, those cases wherein the skeletal atoms involved would be more content in different coordination sites and where, therefore, different deltahedra (with differently coordinated vertices) would be preferred were not considered. However, Wade has deduced that $(CO)_3CrC_6H_6$ is a nido compound (four-coordinate carbon and nine-coordinate chromium) derived from the preferred, in this case, eight-vertex (*154*) hexagonal bipyramid by the removal of one high-coordination vertex.

Wade also incorporates electron-rich species such as $C_5H_5^-$ and $C_4H_4^{2-}$ as arachno species derived by removal of two nonadjacent high-coordination vertices from the pentagonal and tetragonal bipyramids, respectively, and has, moreover, correlated many aspects of seemingly unrelated classes of compounds beyond the recognized borders of carborane chemistry.

When the systems under consideration have additional electrons available for skeletal bonding, fewer bonds are required and the more open, nido and arachno deltahedra fragments describe their structures instead of closed deltahedra.

Of the atoms within the carboranes, the bridge hydrogens (rule 2) are in the most alien environments (as compared to the common one-coordinate terminal hydrogens). Most bridge hydrogens are 100% over their normal coordination environment (two-coordinate), whereas some are 200% over normal (three-coordinate).

The carbons (rule 3) within the carboranes are found in four-, five-, and six-coordinate situations, never over 50% above the normal four-coordinate carbon.

Boron (rule 4) is regarded as most tractable and, therefore, least important; boron has been found to be from three- to seven-coordinate in various molecular configurations.

In discussing the various types and classes of carboranes (*45*, *78*, *123*, *131*, *147*, *147a*, *158*, *164*) in the following sections, the relationship of structure and rule are brought into focus.

III. Carboranes, Their Analogs and Derivatives

A. *closo*-CARBORANES

All of the *closo*-carboranes discovered to date conform to most of the aforementioned rules and were the models from which rules, 1, 3, and 4 were first inferred.

The most stable *closo*-carboranes violate no rules (Fig. 2), whereas a group of slightly less stable *closo*-carborane isomers that will rearrange into the more stable isomers (Fig. 3) violate only rules (3s and 3t). A less stable group of *closo*-carboranes (Fig. 4) is restricted to unfavorable deltahedra, and the least stable known *closo*-carborane (III-C4) violates the very important bridge hydrogen rule (2p) by having a bridge hydrogen of necessity on the cage. Included in Fig. 4 are also selected, and as yet undiscovered, deltahedra.

1. *Stable* closo-*Carboranes*

Before its discovery (and based on CNPR considerations), it was suggested (*172*) that 1,10-$C_2B_8H_{10}$ (I-C2) was destined to be the most stable dicarba-*closo*-carborane (two ideal sites for carbon; eight ideal sites for boron) as has since been confirmed (*137*, *138*). Although the same considerations might apply to an even greater extent to 1,5-$C_2B_3H_5$ (I-C4) (*40*, *126*, *175*), the steric arrangement about carbon (small angles) evidently works against stability in the latter case. The isomers of $C_2B_{10}H_{12}$ (II-C2, III-C2, and II-C3) (*45*, *158*) are less stable than 1,10-$C_2B_8H_{10}$ (I-C2); their carbons would evidently prefer to be less highly coordinated, but within the icosahedral isomers of $C_2B_{10}H_{12}$ that choice does not exist.

Bigger cages, up to but not including seven-coordinate vertices (i.e., less steric strain), tend to accompany increased stability; thus 1,6-$C_2B_4H_6$ (IV-C2) and 2,4-$C_2B_5H_7$ (V-C2) are progressively more stable. Compound $C_2B_6H_8$ (VI-C2) is apparently even more stable and, incidentally, is the only parent *closo*-carborane that is comprised of a *dl*-pair (*172*).

2. *Rearrangement-Prone* closo-*Carboranes*

closo-Carborane isomers that are known to exist and have been isolated but which, upon heating, rearrange into their more stable relatives (Fig. 2), are shown in Fig. 3.

These are not the only rearrangement-prone isomers known to exist. Short-time high-temperature pyrolysis of $C_2B_4H_8$ (III-N6) (*107*) and B_2H_6 produces over 400 compounds, as deduced from gas chromatograph–mass spectroscopic studies (*171*). Although many of the 400 compounds are comprised of the innumerable methyl and polymethyl derivatives of the known carboranes, other compounds that (based on chromatographic retention time and monoisotopic mass spectra) reveal the virtually certain existence of four isomers of $C_2B_5H_7$, six isomers of $C_2B_8H_{10}$, and at least two isomers each of $C_2B_7H_9$ and $C_2B_6H_8$ in addition to myriad others are observed.

Stibr *et al.* (*132a*) have reported the 1,2-isomer of $C_2B_8H_{10}$.

3. *Unstable or Unknown* closo-*Carboranes*

A third group of unstable or unknown *closo*-carboranes is displayed in Fig. 4.

Compounds $C_2B_3H_5$ (I-C4) and 2,3-$C_2B_9H_{11}$ (II-C4) are sterically unfavored closo species that uniquely react with B_2H_6 (*41*) and CH_3Li (*49*) to produce more stable nido counterparts:

$$\textit{closo}\text{-}C_2B_3H_5 + B_2H_6 \longrightarrow \textit{nido}\text{-}C_2B_6H_{10} + H_2$$
$$\textit{closo}\text{-}C_2B_9H_{11} + LiCH_3 \longrightarrow \textit{nido}\text{-}LiCH_3C_2B_9H_{11}$$

The more stable *closo*-carboranes, by contrast (displayed in Figs. 2 and 3), react with these same reagents at higher temperatures to form other *closo*-carboranes or to form dilithio-*closo* derivatives such as $Li_2C_2B_5H_5$ (*169*).

Those species related to $C_2B_9H_{11}$ (II-C4) (*2, 135, 145*) ,i.e., $CB_{10}H_{11}^-$ (*62, 72, 155*) and $B_{11}H_{11}^{2-}$ (*70*), due to the presence of the seven-coordinate boron (violation of rule 4p) tend to scramble their borons on an NMR time scale via a valence bond tautomerism mechanism (*142, 155*) which possibly involves the transient and reversible opening of the eleven-vertex *closo* structure to the eleven-vertex *nido* structure (*55, 96*).

When no carbons are present, i.e., $B_{11}H_{11}^{2-}$, all borons become equivalent on an NMR time scale (*142, 155*). In the case of $CB_{10}H_{11}^-$ (*155*) more restricted scrambling is noted, as the carbon remains in the lowest-coordination position possible, whereas for $C_2B_9H_{11}$ (II-C4) no scrambling is noted as both carbons occupy and remain in the lowest-coordination positions.

It has been implied that open 3-center bonds involving carbon (*142*) inhibit scrambling; more likely, the carbon's predisposition to avoid higher-coordination vertices would inhibit the scrambling mechanism partially in $CB_{10}H_{11}^-$ and completely in $C_2B_9H_{11}$ (II-C4). Should the isoelectronic species, $CH_3B_{11}H_{10}^{2-}$ and $LB{:}B_{11}H_{10}^-$, be formed, less fluxional species might be produced with the methyl group in the former stabilizing a seven-coordinate boron (Table II), whereas the Lewis base would be expected to stabilize one of the five-coordinate sites.

As anticipated (*159*), the structure for $CB_{10}H_{11}^-$, based on rules 3p and 3s, is correct in spite of published ^{11}B NMR data that (*62*) place the carbon in the seven-coordinate position instead of a five-coordinate position.

Onak's CB_5H_7 (III-C4) (*101*) is under investigation by Beaudet (*3*), who has determined that the lone $\overline{666}$-bridge hydrogen is almost certainly above a triangular face. This undesirable situation (a violation of rule 2p) probably accounts for its instability, i.e., in the presence of a Lewis base (proton acceptor) the related *closo*-anion $CB_5H_6^-$ is produced (*116*). More recently, R. R. Rietz has reported (private communication, 1974) a second CB_nH_{n+1} *closo*-carborane, CB_6H_8.

In like manner the presumed intermediate $B_{10}H_{11}^-$ (in brackets in the equation below) would, in the absence of appropriate Lewis bases, probably have the structure VIII-C4; under our reaction conditions, however, it evidently reacts further to produce $B_{10}H_{14}$ (I-N10) and an iodo derivative of I-N10 (*170*):

$$\textit{closo}\text{-}B_{10}H_{10}^{2-} \xrightarrow{+H^+} \textit{closo}\text{-}[B_{10}H_{11}^-] \xrightarrow{+HI} \textit{nido}\text{-}B_{10}H_{12}I^- \xrightarrow{+H^+} \textit{nido}\text{-}B_{10}H_{13}I$$

$$\textit{nido}\text{-}B_{10}H_{13}I + HI \rightleftharpoons \textit{nido}\text{-}B_{10}H_{14} + I_2$$

A. B. Burg suggested that HI would (if it worked) be safer than mixing the borane $B_{10}H_{10}^{2-}$ and a comparable superacid. In a recent communication, Shore (*127*) suggests that a $B_{10}H_{11}^-$ (VIII-C4) salt has been isolated.

Structure IV-C4 is the logical thirteen-vertex polyhedron that would be expected if the L′ process illustrated in the left vertical column in Fig. 1 were simply reversed to generate the next larger polyhedron from the icosahedron. The parent IV-C4 has never been observed, but Dunks *et al.* (*17*, *23*, *26*) have produced derivatives wherein a transition element group occupies one of the two undesirably high-coordinated boron positions. Large polyhedra such as V-C4 or VI-C4 with even more seven-coordinate borons and, thus, susceptible to valence bond tautomerism would also appear to be possible. Perhaps such species will one day be observed as their transition metal-substituted analogs wherein the higher-coordinated vertices are replaced with atoms of transition elements that are more tolerant of seven-coordinate sites than boron. Structure VI-C4 is an alternate choice for V-C4. A unique problem arises when the structure of $C_2B_2H_4$ is considered. If $C_2B_2H_4$ (VII-C4) were to be constructed about the vertices of that deltahedron one vertex smaller than the $C_2B_3H_5$ (I-C4) deltahedron, it should be much more unstable. The degeneracy of the bonding molecular orbitals for tetrahedral $B_4H_4^0$ is such that $B_4H_4^{2-}$ (or presumably $C_2B_2H_4$) is not favored (*48*, *82*).

Just as methyl or alkyl groups tend to stabilize small-ring organic compounds and also $C_2B_3H_5$ [e.g., the $(CH_3)_2C_2B_3(C_2H_5)_3$ (*75*) derivative of $C_2B_3H_5$ is much more stable], perhaps a $H_2C_2B_2(CH_3)_2$ or a $(CH_3)_2C_2B_2(C_2H_5)_2$ derivative of VII-C4 should be sought.

B. *nido*-CARBORANES

Almost all of the *nido*-carboranes have bridge hydrogens, and the organization of their structures is much more complicated than *closo*-carborane structures because the bridge hydrogens (rule 2) apparently outrank the carbons (rule 3) and come into conflict as to low-coordination site preference (*168*).

Among the *nido*-carboranes there are isomers wherein the carbons speciously outrank bridge hydrogens, but they appear to be less stable than isomers that allow the bridge hydrogens to occupy the optimal sites (see rules 2s and 3s in Tables III and IV).

By contrast, within the previously discussed closo-species, CB_nH_{n+2}, only one example [CB_5H_7 (III-C4)] is known; both the lone 666-bridge hydrogen and the carbon could preempt lowest coordination without compromising one another in all members of the series.

Diborane B_2H_6 (with 5′5′-bridge hydrogens) may be considered as the smallest *nido*-borane. Although larger *nido*-boranes such as B_3H_7 and B_4H_8 have been postulated as intermediates, neither has been isolated. The related $B_4H_7^-$ anion (with three 66-bridge hydrogens) has been investigated by Kodama *et al.* (*74*); their suggested most probable tetrahedral structure would seemingly have no obvious site for the additional proton that would be necessary to produce the parent B_4H_8 from the $B_4H_7^-$ anion.

Matteson and Mattschei (*91*) have reported evidence for a CB_3H_7 that should be isoelectronic with $B_4H_7^-$; structural studies should be of great interest.

Plesek and Hermanek have prepared a unique di-*nido*-carborane $C_4B_{18}H_{22}$ (*113e*).

The major *nido*-carborane families are discussed below in the order of increasing complexity.

1. B_6H_{10} *Family of* nido-*Carboranes*

The only complete series of $C_{0-4}B_nH_{n+4}$ *nido*-carboranes is the I-, II-, III-, IV-, IX-N6 series (*158*) displayed in Fig. 6. In this series, the four-coordinate carbons monotonically replace borons about the edge, without compromising the optimal bridge hydrogen positions whatsoever. In the B_6H_{10} family, there need be no competition between bridge hydrogens and carbon for favored positions. Ignoring the presence of bridge hydrogens in Fig. 6, there is, in each structure, 1 six-coordinate apex associated with 5 four-coordinate edge positions. The carbons are ideally four-coordinate in all cases, while the bridge hydrogens (sixty-six- and sixty-five-coordinate in the parent B_6H_{10}) improve (as does the stability) to fifty-five-coordinate in $C_3B_3H_7$ (*9*, *45*). Compound $C_4B_2H_6$ (IX-N6) (*108*, *111*) is extremely stable (no bridge hydrogens); the peralkyl derivative of IX-N6 tolerates hot sulfuric acid without effect (*7*).

Two $C_2B_4H_7^-$ anions, V-N6 and VIII-N6 (*102*), with ideal four-coordinate carbons and 55-bridge hydrogens, have been prepared by Onak *et al.* (*88*, *106*). Two nido Lewis base analogs ($C_2B_4H_6$:LB), VI-N6 and VII-N6 (*88*, *106*) have also been identified. An elegant study by Onak reveals an isomerization wherein the Lewis base in an architecturally compromising situation (i.e., in VII-N6 the Lewis base and a bridge hydrogen are affiliated with the same boron) rearranges or migrates under mild conditions in such a fashion that the undesirable feature is eliminated (VI-N6).

A boron to which is attached a Lewis base is isoelectronic with carbon and thus the Lewis base–bridge hydrogen feature in VII-N6 is undesirable. After the rearrangement the Lewis base is not on the apex (VI-N6), i.e., since it is isoelectronic with carbon it prefers the four-coordinate base site and thus becomes isoelectronic with IV-N6.

Shore (the most prolific producer of new boranes in recent years) has added $B_6H_9^-$ and $B_6H_{11}^+$ to the pantheon of new (N6) boranes (*63*, *64*); the former will be found to have two adjacent 65-bridge hydrogens and a nonadjacent 55-bridge hydrogen whereas in the latter, five 66-bridge hydrogens should be present.

The vacant edge-base bond in B_6H_{10} (I-N6) involves 2 five-coordinate borons; probably the low coordination of the B—B bond (unique among neutral boranes) accounts for both the capacity of B_6H_{10} to act as a Lewis base in accepting a variety of Lewis acids (*63*) as well as the short bond length.

At the other extreme, Hogeveen and Kwant (*59*) have produced the permethyl derivative of $C_6H_6^{2+}$ which is isoelectronic with B_6H_{10}; the cation $C_5BH_6^+$, yet to be described, would be expected to have a similar structure with the boron in the apex position.

2. $B_{10}H_{14}$ *Family of* nido-*Carboranes*

In contrast to the *nido*-B_6H_{10} family, which has only four-coordinate edge positions, the edge positions in the $B_{10}H_{14}$ family are both four- and five-coordinate (disregarding bridge hydrogens), whereas the cage positions are six-coordinate. Thus, in the $B_{10}H_{14}$ family the ideal placement of bridge hydrogens and carbons about the edge may be in conflict.

The known structure of $B_{10}H_{14}$ in both the fluid and crystal phases (*82*) is the structure displayed as I-N10, which incorporates four content 66-bridge hydrogens. For illustrative purposes only, the rotation of the four bridge hydrogens, as displayed in II-N10, would produce two, much less stable, 76-bridge hydrogens and two 75-bridge hydrogens. Not surprisingly, evidence of $B_{10}H_{14}$ in the II-N10 configuration does not exist.

By contrast, consider the two known structures of $B_{10}H_{13}^-$. The III-N10 structure (*129*) optimally minimizes the coordination of the bridge hydrogens and, accordingly, is precisely the structure observed in the unencumbered fluid phase. The 66-bridge hydrogen in $B_{10}H_{13}^-$ (III-N10) occupies a site that is not desirable in the parent $B_{10}H_{14}$ (I-N10) but is desirable in the related anion $B_{10}H_{13}^-$ (III-N10). As in many cases in which hydrogen tautomerism is possible (even probable), a slightly less preferred arrangement is observed in the crystal (*132*) as opposed to the fluid phase. In the encumbered crystal phase, $B_{10}H_{13}^-$ evidently exists as IV-N10, which coincidently reflects the bridge hydrogen placement in the parent $B_{10}H_{14}$ (I-N10). Perhaps a crystal involving another cation would allow the more desirable III-N10 configuration of $B_{10}H_{13}^-$ to be observed even in the crystal phase.

At variance with our view that coordination number considerations are of first-order importance (which favors III-N10), others (*83*, *86*) favor both structures for $B_{10}H_{13}^-$ (III-N10, based on smoother charge distribution, and the IV-N10 structure, based on 3-center resonance considerations). Probably charge and resonance considerations are of importance, and possibly all three considerations are subtly interrelated.

Accenting the premise that bridge hydrogen placement is more important (*32*) than carbon placement leads to the conclusion that the structure V-N10 for the isomers of CB_9H_{13} will be more stable than either VI- or VII-N10. In the latter two cases, a carbon would be in an optimal four-coordination position rather than a five-coordination position (avoiding violating rule 3s), but the bridge hydrogens would suffer high-coordination penalties (violating the more important rule 2s) as a result. The CB_9H_{13} isomer (VI-N10) should be less stable than the parent $B_{10}H_{14}$ (I-N10), whereas the V-N10 isomer of CB_9H_{13} should be of equivalent or greater stability than $B_{10}H_{14}$.

As illustrated in the following sections, there are many examples wherein carbon occupies sites 1 coordination number higher than is otherwise available; but never (to date) has an isomer been observed in which carbon occupies a site that is 2 coordination numbers higher than is otherwise available. Thus, no candidate structures in Fig. 10 are illustrated wherein carbons might be placed in the six-coordination situations when four-coordination alternatives are available. When such isomers are produced they should be less stable than those illustrated and will be cataloged as structures that violate rule 3p.

In contemplating dicarba-*nido*-decaborane species, it is easy to predict the most stable dianion, $C_2B_8H_{10}^{2-}$ (VIII-N10). With no bridge hydrogens to complicate the issue, the most stable isomer should be the isomer illustrated; less stable isomers with carbons in five-coordinate sites should also be observed.

Two isomers of $C_2B_8H_{12}$ have been identified, XX-N10 (*38*) or one of the two bridge hydrogen tautomers, XI- or XVI-N10 (*118*). Because of rule 2s the XI-N10 tautomer should be preferred, but crystal packing forces may favor the XVI-N10 tautomer in the encumbered crystalline phase. Alternatively, in XI-N10 or XVI-N10 [as opposed to $B_{10}H_{13}^-$ (III-N10)] there would be a polarization of the molecule such that the carbon rich end of the molecule would become positively charged and perhaps the bridge hydrogen would tend to migrate toward the relatively negatively charged boron rich zone. XI-N10 and XVI-N10 differ only by the presence of a 65-bridge hydrogen in the former and a 66-bridge hydrogen in the latter.

The known isomers of $C_2B_8H_{12}$ are but two members of a spectrum of six or seven probable isomers yet to be discovered. All are displayed horizontally in Fig. 10 as IX-, X-, XI-, XII-N10 and vertically down the right-hand side of Fig. 10 as XVI-, XX-, and XXIV-N10. Accepting the premise that bridge hydrogen placement is more important than carbon placement suggests that IX- and X-N10 will be the more stable isomers, whereas those at the other end of the spectrum will be less stable.

Identical considerations suggest that the stabilities of the three isomers of $C_3B_7H_{11}$ will decrease in the order XIII- > XIV- > XV-N10. So also the $C_4B_6H_{10}$ isomers should be less stable in the order XVII- (*20, 165*), XVIII-, XIX-N10 (*14*). Brown *et al.* (*14a*), at the University of Liverpool, have shown unequivocally that $H_4C_4B_6(CH_3)_6$ has an adamantane-type structure with sp^2 boron rather than the carborane structure with sp^3 boron.

The *nido*-decaborane and *arachno*-decaborane Lewis base adducts should be discussed in the light of the foregoing considerations. It is well known that the very stable decaborane (I-N10) reacts in excess Lewis base to produce the very stable $B_{10}H_{12}$ (:LB)$_2$ (III-A20); both species violate no rules. It may be presumed that the first step in this sequential transformation is the production of the transient intermediate *arachno*-$B_{10}H_{14}$:LB (II-A20). Such an intermediate, possessing both $\underline{76}'$- and 76-bridge hydrogens should be quite unstable encouraging perhaps the loss of hydrogen which, in turn, would produce *nido*- $B_{10}H_{12}$:LB in either the XXII-N10 (most probable) or XXIII-N10 configurations. Both of these candidate structures have structural handicaps, i..e, 76- and 75-bridge hydrogens are seen in XXII-N10, whereas a bridge hydrogen neighbors a surrogate carbon (a boron to which is coupled a Lewis base) in XXIII-N10. Fortuitously for such species, they have been prepared in the presence of excess Lewis base, and the simple addition of the second Lewis base to either XXII- or XXIII-N10 produces the very stable *arachno*-$B_{10}H_{12}$ (:LB)$_2$ (III-A20) which has content 66-bridge hydrogens and violates no rules whatsoever.

Were this reaction carried out slowly at the lowest possible temperature and in an inert solvent with decaborane in excess rather than with the Lewis base in excess, there might be sufficient time for a Lewis base rearrangement to take place (see rearrangement VII-N6 to VI-N6). The Lewis base could effectively migrate to a higher coordination position and the predicted to-be-stable $B_{10}H_{12}$:LB isomer (XXI-N10) should be produced from the intermediate XXII-N10. Only a 3s violation occasioned by the placement of the surrogate carbon would compromise the XXI-N10 structure for $B_{10}H_{12}$:LB.

An excellent review including research on "the intermediate dicarba-*nido*-boranes" has been compiled by Plesek and Hermanek (*113b*). Many other new compounds are revealed. Previously, they had reported (*113*) the high yield synthesis of 5,6-$C_2B_8H_{12}$ (XI- and XVI-N10).

Stibr *et al.* (*132a*) have reported the nido isomers of $C_2B_8H_{11}^-$ and $C_2B_8H_{10}^{2-}$.

3. B_5H_9 *Family of* nido-*Carboranes*

In the B_5H_9 family (disregarding bridge hydrogens), there is a five-coordinate apex position associated with 4 four-coordinate edge positions. This limited number of edge sites complicates the structures of several isoelectronic analogs of B_5H_9.

A reappraisal of the previously discussed B_6H_{10} and $B_{10}H_{14}$ families reveals the following trends: there is no bridge hydrogen congestion and there are sufficient four-coordinate sites in the B_6H_{10} family (Fig. 6) for carbon substitution without compromising the ideal 66- and 65-sites for bridge hydrogen occupation. The $B_{10}H_{14}$ family (Fig. 10) differed from the B_6H_{10} family in that in accommodating bridge hydrogen coordination number considerations (rule 2s) the carbons, when present, are in cases forced to accept higher five-coordination sites in violation of rule 3s. However, in all of the $B_{10}H_{14}$ family cases the requisite five-coordination sites are available about the open face rather than on the cage or in a cage position.

The B_5H_9 family, by contrast (Fig. 5), is the first case discussed wherein the overriding importance of bridge hydrogen accommodation (i.e., the preempting of edge sites by the bridge hydrogens) forces the carbon into the apex or lone five-coordinate cage position [$C_2B_3H_7$ (IV-N5)]. As far as carbon is concerned, the apex and base positions only differ by 1 in coordination number. At the other extreme, i.e., in the absence of any bridge hydrogens, the occupation of four-coordinate edge positions by all carbons present [e.g., C_4BH_5 (VI-N5)] should be expected.

The pentaborane-type species $C_5H_5^+$ (V-N5) (*89*, *134*, *164*) was discussed in Section I, B.

4. B_9H_{13} *Family of* nido-*Carboranes*

The next family to be discussed, i.e., the nine-vertex *nido*-carboranes, includes the complications of the $B_{10}H_{14}$ family (i.e., differingly coordinated edge positions) as well as one additional complication not encountered in the B_6H_{10}, $B_{10}H_{14}$, and B_5H_9 families. The additional perturbation arises when a selected cage position and certain edge positions are of equivalent coordination number (disregarding bridge hydrogens).

In the previous paper (*164*) the difficulties of placing four bridge hydrogens about the unfavorably puckered five-membered face of the preferred nine-vertex nido fragment was pointed out; thus the polyhedral fragment displayed in Fig. 9 for B_9H_{13} (I-N9) should be unstable due to extensive bridge hydrogen congestion. Three of the four bridge hydrogens (77-, 76-, 76-) in I-N9 are also overly coordinated. The simple removal of the acutely offensive 77-bridge hydrogen to produce $B_9H_{12}^-$ (II-N9) removes all objections simultaneously, i.e., removes bridge hydrogen crowding and generates three compliant 66-bridge hydrogens. During the preparation of this manuscript, Siedle *et al.* (*128*) furnished precisely the ^{11}B and ^1H NMR spectra that are required by the numbers and kinds of hydrogens and borons (six types of boron in the ratio of 2:2:2:1:1:1) for the projected structure for $B_9H_{12}^-$ (II-N9) (*164*). In other words, the B_9H_{13} structure (I-N9) should not be stable (considering bridge hydrogen congestion and coordination number); however, the anion, $B_9H_{12}^-$ (II-N9), differing by only one bridge hydrogen, should be stable. Were $B_9H_{12}^-$ related to III-N9, bridge hydrogen tautomerism would have resulted in three kinds of boron in the ratio of 3:3:3.

In Fig. 9, there is an alternative III-N9 structure for the parent borane, B_9H_{13}. Such a structure, formed by the breaking of one high coordination bond, produces in I-N9 the skeletal arrangement characteristic of *i*-B_9H_{15} (I-A19), i.e., an arachno structure rather than the nido structure (I-N9). The III-N9 structure may be more probable than the I-N9 structure and has the precedent of B_8H_{12} (I-N8) which incorporates 76-bridge hydrogens preferring, by the breaking of one high-coordination bond, the III-N8 structure (involving only 66-bridge hydrogens) characteristic of the *arachno*-borane B_8H_{14} (I-A18), at least in the crystal phase. However, in the case of B_9H_{13} (III-N9), undesirable 76- and 75-bridge hydrogens remain, even following the "nido to arachno" transformation (suggestive of instability). It seems that structure III-N9 for B_9H_{13} has "one strike against it" but may be more promising than I-N9.

Amplifying the difficulties in selecting a satisfactory structure for B_9H_{13}, consider the following: for every electron that is deficient there should be one 3-center bond (*82*) involving either three borons, two borons and a carbon, or two borons and a hydrogen (i.e., a bridge hydrogen).

In a given molecular system the total number of 3-center bonds will be dictated by the empirical formula with an ideal number expressed within the cage, whereas if extra hydrogens are present they may be expressed as bridge hydrogens.

What would happen if the "idealized" structure for B_9H_{13} (I-N9), which should have a total of nine 3-center bonds, opened to produce the III-N9 structure to avoid bridge hydrogen congestion? We suggest that, since nine 3-center bonds are present in any case, the open III-N9 structure would be less hospitable to the five, required, skeletal 3-center bonds than would be I-N9. The four extra 3-center bridge hydrogens would, in both cases, account for the other four electrons that are deficient. Since there are no other extra hydrogens, i.e., endohydrogens, to be impressed into service as bridge hydrogens, the structure III-N9 has no recourse but to account for the requisite five electrons deficient by somehow including five 3-center bonds within the more open skeleton.

Consider the further iniquity of converting two of the four 3-center bridge hydrogens (in III-N9) into endohydrogens. With only two 3-center bonds consequently allowed to be expressed as 3-center bridge hydrogens, "conservation of 3-center bonds" would require that seven instead of five 3-center bonds would have to be expressed within the already sundered skeleton.

The probability of four-center or five-center bonds completely accounting for the skeletal electron deficiencies in the B_9H_{13} structure (IV-N9) is a probability that must be rejected. Structure IV-N9 for B_9H_{13} is extremely unlikely. By contrast, others have described the same B_9H_{13} structure (IV-N9) as "eminently satisfactory" (*83*, *86*). This is but one of several examples that illustrate the diametrically opposing predictions resulting from other theories as compared to CNPR theory.

When contemplating potential $C_2B_7H_{11}$ carborane isomers, as displayed horizontally in the middle row of Fig. 9, and noting that in contrast to the B_6H_{10}, $B_{10}H_{14}$, and B_5H_9 families (Figs. 6, 10, and 5), one cage position in the nine-vertex nido species has a coordination number as low as four of the five positions around the open face, the five-coordinate cage position and edge positions should be considered as equivalently satisfactory for carbon's occupancy. Again, based on the greater demand of bridge hydrogens than that of carbons for lower-coordination environments, we predict that the various isomers displayed for $C_2B_7H_{11}$ would decrease in stability in the order VI- > VII- > VIII- > IX- > X-N9, whereas isomer V-N9 would be predicted to be the least stable (one unstable isomer containing 76- and 75-bridge hydrogens is not shown). Following the patterns and parallels discussed above involving the $C_2B_8H_{12}$ isomers in Fig. 10, it is easy to follow the reasons for the predicted order of stability.

A *C*,*C*-dimethyl isomer of $C_2B_7H_{11}$ has been identified (*118*) and is displayed as IX-N9 (X-ray crystal structure) (*61*). The bridge hydrogen tautomer of IX-N9 (i.e., VII-N9) should be observed in the unencumbered fluid phase to minimize the bridge hydrogen coordination numbers.

Near the completion of this manuscript, Rietz and Schaeffer revealed (*119*) that the parent compound $C_2B_7H_{11}$ almost certainly does not have the same structure as the *C*,*C*-dimethyl derivative which has the structure IX-N9. It is interesting to note that a BH_2 group is present in the parent $C_2B_7H_{11}$ that is not present in the *C*,*C*-dimethyl derivative (IX-N9). The authors suggest, as one candidate, a structure similar to the XIII-N9 configuration with one of the 65-bridge hydrogens in XIII-N9 biasing completely to the five-coordinate boron thus producing a five-coordinate BH_2 group. This structure may be correct yet there are several alternatives.

The presence of BH_2 groups in nido species, e.g., $B_{11}H_{15}$ (II-N11) and the unstable isomer of $C_2B_9H_{13}$ (not shown) is a possibility that has not been rejected. And as will be seen below under the discussion of the *arachno*-boranes B_5H_{11} (I-A15 versus II-A15) and $B_9H_{14}^-$ (V-A19 versus VI-A19), bridge hydrogen versus endohydrogen status is not considered sacred; in fact, a continuum of BE hydrogens is preferred. Yet both of the two hydrogens in the BH_2 group (in the parent $C_2B_7H_{11}$) spin couple to the boron with exactly the same coupling constant ($J = 125$ cps), which should not be expected in any "XIII-N9-like" structure. As mentioned earlier, the concept of conservation of 3-center bonds with regard to the opening of a nido structure into an arachno structure and the concurrent conversion of a bridge hydrogen into an endohydrogen, is considered to be electronically improbable paralleling the arguments advanced against structure IV-N9 for B_9H_{13} (above).

The acceptance of an N9 structure (necessarily incorporating vicinal carbons) in accordance with rules 1–4 would favor a VII-N9 structure for the parent $C_2B_7H_{11}$ with the 65-bridge hydrogen converting into an endohydrogen (to produce a five-coordinate BH_2 group). Such a structure is unlikely because the presence of two methyl groups (on remote carbons) would not be expected to cause the "extra hydrogens" to occupy different sites.

The following thoughts suggest an alternate structure. The highly symmetrical triplet in the ^{11}B NMR spectrum is reminiscent of the BH_2 groups in B_5H_{11} (I-A15) and B_4H_{10} (I-A14). In those cases the two "different" terminal hydrogens of the BH_2's neighbor one or two bridge hydrogens and are presumed to become NMR equivalent by rapid fluxional behavior on an NMR time scale. Consider also that μ-$(CH_3)_2BB_5H_8$ exists (*36*, *37*) and may be considered as either a derivative of B_5H_9 or B_6H_{10} (see X-N5 or X-N6, both in Fig. 7); i.e., a precedent for a dialkyl-substituted BH_2-containing *nido*-borane exists.

A μ-BH_2 or a μ-BH_2H derivative of a $C_2B_6H_{10}$ isomer (i.e., μ-$BH_2HC_2B_6H_8 \cong C_2B_7H_{11}$) might account for the data. Such a compound (not shown) could resemble one of the $C_2B_6H_{10}$ structures in Fig. 8 with an added BH_3 group (two terminal hydrogens and one neighboring bridge hydrogen) replacing both bridge hydrogens and resembling VII-N7. The carbons could be vicinal in any number of ways; the fluxional BH_2 group would account for the precisely equivalent coupling, and, since the parent $C_2B_7H_{11}$ and the dimethyl derivative of $C_2B_7H_{11}$ (with the known structure IX-N9) would not be isoelectronic, the radically different ^{11}B and ^{1}H NMR spectra would be explained.

The BH_3 groups may be removed from similar species such as B_2H_6, B_4H_{10}, and B_5H_{11}; thus the parent *nido*-$C_2B_7H_{11}$ might provide an easy route to a new closo isomer of $C_2B_6H_8$ with adjacent carbons by similar loss of a BH_3 group. Subsequently, R. R. Rietz reported (private communication, 1974) the isolation and identification of 1,2-$C_2B_6H_8$ from the parent $C_2B_7H_{11}$ in about 12% yield.

Of the several $C_2B_7H_9^{2-}$ isomers, XI- and XII-N9 are predicted to be most stable; carbon in these cases would be expected to occupy the lone four-coordinate position. In a similar vein, the $C_4B_5H_9$ isomers XIV- and XV-N9 would be expected to be stable although other stable $C_4B_5H_9$ isomers are possible.

5. *B_7H_{11} Family of* nido-*Carboranes*

Only a few comments need be expended relative to this group of *nido*-carboranes since, as far as is known, *no species such as B_7H_{11} or any species isoelectronic with B_7H_{11} (I-N7) has ever been reported.* On first principles we would select I-N7 as the structure for B_7H_{11}; however, partially paralleling the situation for B_9H_{13} (I-N9), there are undesirable 75- and 76-bridge hydrogens in addition to the probable bridge hydrogen congestion. The removal of one bridge hydrogen to generate $B_7H_{10}^-$ (V-N7) seemingly could alleviate both of these problems; perhaps the V-N7 structure may one day be observed. It has been predicted (*84*) that B_7H_{11} would have the structure II-N7 produced by simultaneously opening up the I-N7 structure and converting two bridge hydrogens into endohydrogens. Paralleling the arguments advanced against the B_9H_{13} structure IV-N9, the II-N7 configuration (*84*) for B_7H_{11} is extremely improbable.

A more likely structure for B_7H_{11} is displayed as VIII-N7 and is related to either X-N5 (*36*, *37*) (μ-$BH_2B_5H_8$) or X-N6 (both shown in Fig. 7). There is no doubt that a dimethyl derivative of either X-N5 or X-N6 (both shown in Fig. 7) has been produced which, upon heating, reverts to the dimethyl derivative of B_6H_{10} (I-N6) (*37*). The suggested VIII-N7 structure for *i*-B_7H_{11} would bear the same relationship as X-N6 to *i*-B_6H_{10} (i.e., minimize bridge hydrogen coordination numbers) or as X-N5 would bear to B_5H_9 (I-N5).

Reasonable 3-center bond descriptions of both *i*-B_6H_{10} (X-N6) and *i*-B_7H_{11} (VIII-N7), however, are not obvious; thus μ-$BH_2B_5H_8$ (X-N5) is favored as well as a similar μ-$BH_2B_6H_9$ structure for B_7H_{11}.

Six hypothetical isomers of $C_2B_5H_9$ are displayed and, for reasons similar to those invoked in the cases of $C_2B_7H_{11}$ and $C_2B_8H_{12}$ (in Figs. 9 and 10), the isomer III-M7 should be anticipated to be most stable, whereas isomer X-N7 would be the least stable. The isomer of $C_2B_5H_7^{2-}$ predicted to be the most stable and the two isomers of $C_4B_3H_7$ expected to be most stable are displayed as XI-, XII-, and XIII-N7, respectively.

6. [B_8H_{12}] *Family of* nido-*Carboranes*

The known structure of the *nido*-borane B_8H_{12} in the crystalline state (*82*) has been determined to be III-N8, which is in contrast to the preferred B_8H_{12} nonicosahedral structure (I-N8) (*164*) and is similar to the eight-vertex arachno species displayed in Fig. 18. Perhaps the two 76-bridge hydrogens in I-N8 militate against stability (since there would be no bridge hydrogen crowding). It was thought that perhaps an isoelectronic carborane derivative such as $C_2B_6H_{10}$ with two fewer hydrogens of lower-coordination number might assume the literal nido structure, e.g., X-N8.

Since a rather unstable $C_2B_6H_{10}$ *nido*-carborane had been known for several years to exist, this isomer of $C_2B_6H_{10}$ was structurally identified (*41*) as having (probably) the arachno structure of V-N8 instead of the nido structure X-N8, but this is not yet sure.

Structure X-N8 differs from V-N8 by only one high-coordination edge bond and the presence or absence of such a bond would not affect the coordination numbers of either carbon. There is no precedent to indicate that the more desirable 55-bridge hydrogens in V-N8, as opposed to the 65-bridge hydrogens in X-N8, would constitute a sufficient driving force for opening into the arachno configuration. If the X-N8 structures were actually a pair of valence bond tautomers, i.e., the unique edge bond alternating positions between the two borons as shown in X-N8 and X′-N8 (rapidly on an NMR time scale), then the data could also be rationalized in terms of a valence bond tautomeric pair.

Perhaps the B_8H_{12} structure I-N8 and the $C_2B_6H_{10}$ structure X-N8 will be found to be preferred in the fluid phases. Microwave and/or electron diffraction studies of B_8H_{12} and $C_2B_6H_{10}$ in the unencumbered vapor phases are in progress and should adjudicate this structural dilemma. In any case the assumption of either the V-N8 or X-N8 structures (both ideal for bridge hydrogens) rather than alternatives that would be ideal for carbons is again indicative that accommodating the bridge hydrogens (rule 2s) is more important than accommodating the carbons (rule 3s).

It would appear that rule 1 correctly predicts the structures of all nido species (see Fig. 1) except perhaps the structures of the eight-vertex nido species that, at least in the two cases known, tentatively seem to assume the arachno configuration. Candidate structures for $C_4B_4H_8$ are XI-, XII-, and/or IX-N8; the most probable candidate for a true nido structure is VIII-N8 ($C_2B_6H_8^{2-}$).

When the conservation of 3-center bondedness relating to B_9H_{13} (III- or IV-N9) was discussed, the penalty for opening up the skeletal framework by the breaking of an edge bond was pointed out to be that of greater difficulty in harboring the required number of 3-center bonds. Possibly the eight-vertex nido compounds have a singular electronic solution to this dilemma and can uniquely accept the requisite four 3-center bonds within an arachno-skeletal framework. As a possible precedent, the eleven-vertex closo compound $CB_{10}H_{11}^-$ seems (at least transiently) to open reversibly into an eleven-vertex nido structure (*155*). In any event, none of the bridge hydrogens in B_8H_{12} (III-N8) are converted into endohydrogens which is the greatest criticism of IV-N9 for B_9H_{13} and II-N7 for B_7H_{11}.

7. [$B_{11}H_{15}$] *Family of* nido-*Carboranes*

Compound $B_{11}H_{15}$ has had a checkered history; it may have been prepared (*28*), but probably not. The straightforward structure would be I-N11 (incorporating four bridge hydrogens and seven skeletal 3-center bonds) but the presence of two $\overline{77}$- and two 76-bridge hydrogens (also very congested) should render such a species very unstable. Conversion of one bridge hydrogen into an endohydrogen (II-N11) would produce a six-coordinate BH_2 group (violation of rule 4p) and would require an eighth 3-center bond to be expressed within the skeletal framework (more acceptable in larger frameworks), but would still leave one very undesirable 77- and two 76-bridge hydrogens; these are very unsatisfactory solutions. Perhaps an edge bond breaks (not shown, but similar to II-A21 and paralleling the situation with B_8H_{12}; i.e., the preferred CNPR I-N8 structure opens into the III-N8 structure) which would produce a six-membered, favorably puckered open face with additional room for the four bridge hydrogens. Although the problem ought to be less serious with larger molecules, the opening should make a less favorable environment for the requisite, seven, skeletal 3-center bonds and three 7X-bridge hydrogens would remain. Removal of a single bridge hydrogen from I-N11 produces $B_{11}H_{14}^-$ (III-N11) (*1*) which is stable in spite of its compromising 76-bridge hydrogens, but then the negative charge probably furnishes the attraction to keep the two 76-bridge hydrogens content. An alternative (not shown) with a six-coordinate (violates rule 4p) BH_2 group and two 66-bridge hydrogens must also be considered for $B_{11}H_{14}^-$. Moreover *nido*-$B_{11}H_{14}^-$ may always be associated with at least one Lewis base [e.g., $B_{11}H_{14}$ (:LB)] which would relate to it *arachno*-$B_{11}H_{16}^-$ in Fig. 21. The seven-coordinated boron would facilitate fluxional behavior and account for the single kind of boron seen in the ^{11}B NMR spectrum of $B_{11}H_{14}^-$ in etherial solution. When two bridge hydrogens are removed from $B_{11}H_{15}$ to produce $B_{11}H_{13}^{2-}$ (IV-N11) (*1*, *34*), a very stable species that incorporates two content 66-bridge hydrogens is obtained.

One of the two isomers of $C_2B_9H_{13}$ is also in question; the known marginally stable isomer of $C_2B_9H_{13}$ (V-N11) (*60*, *160*) has adjacent carbons and adjacent 76-bridge hydrogens. Attempts to isolate the less stable isomer (presumably with nonadjacent carbons) have failed.

A structure for the less stable isomer of $C_2B_9H_{13}$ with nonadjacent carbons about the open face incorporating one 66-bridge hydrogen and one endohydrogen on the boron between the carbons (a violation of rule 4p) might possibly be correct or, perhaps, one edge bond breaks between the carbons (see IX-N11) which would allow the introduction of a 75-bridge hydrogen into a "II-A21-like" structure.

A likely candidate structure for an even more stable isomer of $C_2B_9H_{13}$ is VI-NII (*161*), which only violates rule 3s and has content 66-bridge hydrogens; other variants with carbon in cage positions are probable. Another isomer of $C_2B_9H_{13}$ has been prepared from 1,12-$C_2B_{10}H_{12}$ (II-C2). The structure (*113a*) resembles VI-N11; however, the cage carbon is para to the edge carbon rather than meta. Furthermore, Rietz (private communication, 1974) has also detected a second, more stable isomer of $C_2B_9H_{13}$ from the pyrolysis of $C_2B_7H_{11}$. A structure with one carbon in a six-coordinate cage position (violation of 3s) but with content 66-bridge hydrogens (resembling VI-N11 or VIII-N11) should be suspected.

Two isomers of $CB_{10}H_{13}^-$ are known: VII-N11 (*140*, *160*) and the less stable isomer VIII-N11 (*6*), which incorporates one 3s violation.

If VIII-N11 ($CB_{10}H_{13}^-$) were neutralized to $CB_{10}H_{14}$, then it might be more acidic than $B_{11}H_{14}^-$ (III-N11) since the negative charge in the latter should result in more content 76-bridge hydrogens. Lewis base analogs of the $C_2B_9H_{12}^-$ isomer (IX-N11) have been prepared from $C_2B_9H_{11}$ (II-C4) by Chowdhry *et al.*; the bridge hydrogens are found about the open face but the Lewis base group in *nido*-LB:7,9-$C_2B_9H_{11}$ is found upon the cage (violation of rule 3s) (*16*).

The bridge hydrogens in the isomers of $C_2B_9H_{12}^-$ (IX-N11 and X-N11) are positioned (*60*) exactly as previously suggested (*160*). In the absence of complicating bridge hydrogens, the related species such as the two obvious isomers of $C_2B_9H_{11}^{2-}$ and $C_4B_7H_{11}$ (XI-N11) (*20*) are very stable.

Plesek *et al.* (*113d*) have prepared the nido compound $NC_2B_8H_{11}$ which is isoelectronic with $C_4B_7H_{11}$ (XI-N11). They suggest a CHBH-NHBHCH pentagonal open face, and, since the nitrogen donates two electrons (see Section III, E) and, consequently, becomes quite positively charged, we would anticipate their reported anion $NC_2B_8H_{10}^-$ would differ from the parent by simply lacking the most acidic nitrogen-attached proton. They also reported an $NC_2B_8H_{13}$ which they show is a derivative of 5,6-$C_2B_8H_{12}$ with a bridging NH_2 group.

8. [$B_{12}H_{16}$] *Family of* nido-*Carboranes*

Were *nido*-$B_{12}H_{16}$ (I-N12) to be discovered, it would be expected to have the basic skeletal structure of the most probable thirteen-vertex closo polyhedron as typified by $C_2B_{11}H_{13}$ (IV-C4), with one of the 2 seven-coordinate vertex positions removed and embracing four bridge hydrogens (I-N12) about the perimeter in the lowest possible coordination situations. As a consequence of the presence of a seven-coordinate BH group, wholesale bridge hydrogen and valence bond tautomerism should be expected; quite possibly the ^{11}B NMR spectra of $B_{12}H_{16}$ or of related anions such as $B_{12}H_{15}^-$ or $B_{12}H_{14}^{2-}$ would be simple doublets at ambient temperatures.

It has been noted by workers in both the USSR (*178–181*) and United States (*24*, *31*, *42*) that all closo isomers of $C_2B_{10}H_{12}$ (II-C2, III-C2, and

II-C3) add two electrons to become the corresponding *nido*-$C_2B_{10}H_{12}^{2-}$ dianions which would be isoelectronic with $B_{12}H_{16}$ and which should have skeletal structures resembling I-N12.

An attempt to relate the known closo-icosahedral "parents" to their nido twelve-vertex progeny follows.

Since the two carbons in 1,2-$C_2B_{10}H_{12}$ (II-C3) are furnishing the two extra electrons (as compared to $B_{12}H_{12}^{2-}$), any overall dipole should have its positive center "between" the carbons. Moreover, since the closo structure, upon opening into a nido structure, should preferably have its carbons about the resulting open face, the most likely electron-deficient recipients of any additional electrons would be those borons neighboring the carbons, which would become surrogate carbons upon receipt of electrons. Compound 1,2-$C_2B_{10}H_{12}$ (II-C3) possibly accepts two electrons to produce the hypothetical intermediate (II-N12) which by one dsd rearrangement (involving the carbon–carbon bond) would produce the transient intermediate (III-N12).

There is a special and very important feature of the anticipated open nido twelve-vertex structures in Fig. 12: repetition of single Lipscomb dsd rearrangements (denoted by the two-headed arrows) monotonically allows the six skeletal atoms about the open face to rotate about the second tier of five skeletal atoms (two-tier dsd rotation). Each dsd rearrangement (*85, 163*) (valence bond tautomerism) recreates the same configuration and involves only the motion of two skeletal atoms (in the ball-and-stick representation) and would allow carbons, if located in different tiers, to migrate apart. Such wholesale valence bond tautomerism is known to accompany the presence of seven-coordinate BH groups, e.g., $B_{11}H_{11}^{2-}$ and $CB_{10}H_{11}^{-}$ (*142, 155*).

In order to place at least one carbon in the lowest-coordination edge position, configuration III-N12 would tend to rearrange into the preferred IV-N12 by a single dsd rearrangement. Rapid fluxional behavior, engendered by the presence of the seven-coordinate boron which, utilizing the intermediate (III-N12), would make the CH groups in IV-N12 equivalent on an NMR time scale, should be anticipated. Upon reoxidation the reverse process, i.e., IV-N12 → III-N12 → II-N12 → II-C3, would take place and thus the original 1,2-$C_2B_{10}H_{12}$ would be produced.

Turning to 1,7-$C_2B_{10}H_{12}$ (III-C2), the addition of electrons, again between the carbons, should produce the hypothetical intermediate (VI-N12) which would rearrange into the intermediate VII-N12 via a single dsd permutation and finally rearrange into IV-N12 (to accommodate carbon preference); Structure IV-N12 is thus exactly the same species as is produced from 1,2-$C_2B_{10}H_{12}$. In this fashion the experimental observations that both 1,2- and 1,7-$C_2B_{10}H_{12}$ produce, upon reduction, the same $C_2B_{10}H_{12}{}^{2-}$ anion and produce only 1,2-$C_2B_{10}H_{12}$ upon reoxidation may be rationalized.

Compound 1,12-$C_2B_{10}H_{12}$ (II-C2) does not have the same options available as the 1,2- and 1,7-isomers (all borons are equivalent), and the configurational sequence, 11-C2 → [X-N12] → [XI-N12] → [XII-N12] → [XIII-N12], is envisaged as most probable. In these fluxional species, two-tier dsd rearrangement would account for the production of the intermediate XII-N12 structure from XI-N12 were it necessary. Were the second carbon trapped within or restricted to the second tier (a violation of rule 3p), then the position farthest away from the seven-coordinate boron would be the best position for the second carbon (i.e., XII-N12). Actually, carbon would prefer to be about the open face, which suggests that the ideal carbon positions upon the twelve-vertex nido skeleton would be those displayed in XIII-N12 and, given the fluxional characteristics that accompany seven-coordinate BH groups, intermediate XII-N12 should be able to rearrange into the more stable XIII-N12 isomer. Reoxidation of XIII-N12 would move any one of the four edge borons (probably all four are equivalent on an NMR time scale) into an apex position thus producing 1,7-$C_2B_{10}H_{12}$ (III-C2) from 1,12-$C_2B_{10}H_{12}$ (II-C2), exactly as is experimentally known to be the case.

In summary, the reduction–oxidation of both 1,2- and 1,7-$C_2B_{10}H_{12}$ to produce 1,2-$C_2B_{10}H_{12}$ and the reduction–oxidation of 1,12-$C_2B_{10}H_{12}$ to produce only 1,7-$C_2B_{10}H_{12}$ can tentatively be accounted for on a structural basis.

Were a proton added to the $C_2B_{10}H_{12}{}^{2-}$ dianion IV-N12 (derived from either 1,2-$C_2B_{10}H_{12}$ or 1,7-$C_2B_{10}H_{12}$), the $C_2B_{10}H_{13}{}^{-}$ anion V-N12 should be anticipated, and one carbon should be expected to defer to the bridge hydrogen preference. Whether the added proton becomes a tautomerizing bridge hydrogen or an endohydrogen is probably unimportant; similar protons are observed in $B_9H_{14}{}^{-}$ (V-A19 vs. VI-A19) and in B_5H_{11} (I-A15 vs. II-A15). But since there are no triplets in the ^{11}B NMR spectrum, the V-N12 structure incorporating a bridge hydrogen is favored in the fluid phase.

If a proton is added to the dianion XIII-N12 (derived from 1,12-$C_2B_{10}H_{12}$), CNPR rules suggest that a $C_2B_{10}H_{13}{}^{-}$ anion with the structure VIII-N12 should be expected. However, since NMR data indicated that the "extra" proton is on the carbon, the pseudoicosahedral fragment structure (IX-N12), known to be correct in the crystalline phase, must be accepted as correct even in the fluid phase (*24*, *141*).

A previously disturbing feature of the published ^{11}B NMR spectra

(*24*) of the two $C_2B_{10}H_{13}^-$ anions was that they appeared sufficiently different not to be representative of isoelectronic species. Thus, the finding (*141*) that IX-N12 has a "bridging" CH_2 group and is more of an N11 derivative than an N12 compound eliminates this dilemma: the two ions are not isostructural and, therefore not isoelectronic. That is not to say that $C_2B_{10}H_{13}^-$ (IX-N12) is an alkyl derivative of $CB_{10}H_{13}^-$ (VII-N11), however, because evidently no bridge hydrogens are generated.

Were electron exchange possible (i.e., $C_2B_{10}H_{12} + C_2H_{10}B_{12}^{2-} \rightleftharpoons C_2B_{10}H_{12}^{2-} + C_2B_{10}H_{12}$) then, in the presence of any unreacted $C_2B_{10}H_{12}$, structure XIII-N12 would be expected to slowly convert into IV-N12 as has been observed (*24*) experimentally.

Wade points out that Wing's "slipped" dicarbollide species (*176*) such as $Cu(C_2B_9H_{11})_2$ could be considered as a dinido species, each $CuC_2B_9H_{11}$ unit filling twelve of the vertices of the thirteen-vertex polyhedron typified by IV-24.

C. *arachno*-CARBORANES

The *arachno*-carboranes and their analogs may be discussed in somewhat less complicated terms than their nido relatives. The trend is as follows: in the *closo*-species there are no endohydrogens and there are a sufficient number of low-coordination sites so that the bridge hydrogen and the carbon need not be in competition. In the nido species, endohydrogens are also generally absent but there are more bridge hydrogens or carbons, and complicated competition between bridge hydrogens and carbon for low-coordination sites is pervasive. By contrast, within the arachno species, endohydrogens are usually present and carbons (reluctantly), when also present, frequently collaborate with the endohydrogens in occupying the lowest-coordination sites together. Thus, instead of bridge hydrogens and carbons competing for lowest-coordination sites, as in the nido species, frequently the endohydrogens and carbons appear to occupy jointly the lowest-coordination sites within the arachno species to accommodate the endohydrogen preferences.

Among the *arachno*-boranes, it would appear to date that the bridge hydrogens are more acidic than the endohydrogens of five-coordinate BH_2 groups, but that the endohydrogens of five-coordinate CH_2 groups are more acidic than the bridge hydrogens. As is discussed in more detail in Section IV, the proton acidity among the *arachno*-carboranes and related species is, in the order of increasing acidity, BHB bridge hydrogen < endo CH (above four-coordinate) < endo NH $\simeq$ SH. Thus anion formation involves the loss of bridge hydrogens in the *arachno*-boranes, e.g., $B_{10}H_{15}^-$ (*122*) to form $B_{10}H_{14}^{2-}$ and B_4H_{10} to form $B_4H_9^-$ (*65*), as opposed to loss of endo heteroatom hydrogens to produce $C_2B_7H_{12}^-$ (*136*) and $SB_9H_{12}^-$ (*57*) etc., when *arachno*-carboranes or heteroatom *arachno*-boranes are involved.

Inasmuch as bridge hydrogens and endohydrogens are considered to constitute a continuum (e.g., some "extra" hydrogens are pure endo, some pure bridge, and some in between with characteristics of both), it should not be surprising that among the *arachno*-boranes there are several conflicts as to whether selected extra hydrogens are endo or bridge and that, in the encumbered crystal phase packing forces may sometimes cause a bridge hydrogen to become an endohydrogen or vice versa.

The smallest *arachno*-borane is apparently $B_2H_7^-$ (*13*, *35*, *58*) with a 4″4″- or a 5″5″-bridge hydrogen, stabilized by the presence of the negative charge.

1. [B_3H_9] Family of arachno-*Carboranes*

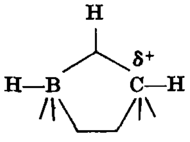
The parent B_3H_9 (V-A13) has apparently never been observed. This probably results from the presence of three 6′6′-bridge hydrogens accompanied by the 3 six-coordinate BH_2 groups. Disproportionation of B_3H_9 into B_2H_6 is favored as more content 5′5′-bridge hydrogens and five-coordinate BH_2 groups are produced.

The removal of one bridge hydrogen from B_3H_9 (V-A13) produces $B_3H_8^-$ (I-A13) (*82*), incorporating marginally acceptable 6′5′-bridge hydrogens. The acidic nature of the 6′5′-bridge hydrogens is probably sated by the compensating presence of the negative charge.

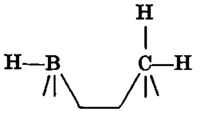
For illustrative purposes an alternative structure for $B_3H_8^-$ should be compared. For example, could not one bridge hydrogen in I-A13 become a terminal hydrogen as depicted in VI-A13? Such a configuration would violate rule 4p but the remaining 5′5′-bridge hydrogens should be more content. At least in the encumbered crystal phase, the $B_3H_8^-$ structure (I-A13) is observed; perhaps the "almost-as-satisfactory" alternative VI-A13 facilitates the capacity for tautomerism, known to be rampant in this ion in the liquid phase.

In the isoelectronic B_3H_7:LB species, the liquid phase structure (VII-A13) is definitely indicated to be correct by Parry and Paine (*39*, *109*), rather than a structure with elements of both VII-A13 and II-A13 which may be more stable in the crystal phase (*97*).

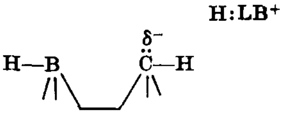
At this juncture it is useful to consider the situation that would obtain were a bridge hydrogen neighboring a carbon (CH group) or a surrogate carbon (i.e., a B:LB group). A carbon donating electrons into an electron-deficient sink (as in a carborane) would, as a result, become positively charged as shown in structure a; this situation would be partially alleviated if the carbon preempted the neighboring bridge hydrogen and the electrons involved structure b and even more so if the carbon preempted the neighboring bridge hydrogen and the electrons involved and then released the proton while retaining the two electrons (structure c). Such a proton could perhaps relocate elsewhere on the molecule as is illustrated in Section III, E.



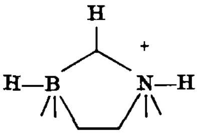
(a)



(b)



(c)



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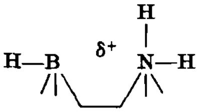
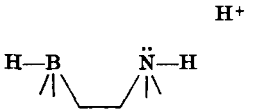


(e)



(f)

This sequence parallels, first, the reasons bridge hydrogens tend not to neighbor carbons (or borons that are attached to Lewis bases), second, the reasons CH_2 (or BH:LB) groups are preferentially found among the *arachno*-carboranes, and, third, the reasons that when such species produce anions, the endohydrogens of CH_2 groups are the most acidic. In seeming support of this, were a nitrogen in a similar environment and, thus, required to donate twice as many electrons as carbon, the nitrogen involved should reflect to a greater extent the trends observed with carbon. Indeed, as is seen in Section III, E and in Fig. 25, not only has a bridge hydrogen neighboring a nitrogen never been observed (structure d) but the hypothetical endohydrogen of an NH_2 group (structure e) is evidently too acidic to remain on nitrogen and only arachno species with NH groups (structure f) are to be anticipated under normal circumstances. Superacids or liquid hydrogen iodide might produce species incorporating NH_2 or isoelectronic SH groups from their related anions.

The picture becomes somewhat more complete when the structural choices available for the $C_3H_7^+$ cation are considered. This species is known as its trialkyl derivative, norbornyl cation (*99*). It has been unequivocally demonstrated by NMR spectra that the extra hydrogen in norbornyl cation assumes an endo position (VIII-A13). A good way to view the $C_3H_7^+$ alternatives is to recognize that one 3-center bond is mandatory and that the 3-center bond could be expressed as (*a*) and CHC-bridge hydrogen (III-A13) or, more likely, as either (*b*) a 3-center bond involving the three carbons (CCC) or (*c*) a CHH 3-center bond involving two of the three terminal hydrogens in the CH_3 group of VIII-A13. The CCC 3-center bond alternative (*b*) is preferable since it distributes the necessarily present positive charge among the three carbons rather than involving less tolerant hydrogens. And just as the negative charge could stabilize the 6′5′-bridge hydrogens in $B_3H_8^-$ (I-A13), it is likely that the positive charge in $C_3H_7^+$ would militate against stability of a 5′5′-bridge hydrogen in III-A13.

Probably the CH_3 group in $C_3H_7^+$ (VIII-A13), the bridging CH_3 groups in $(CH_3)_6Al_2$, and the bridging LB:BH_2 groups in LB:B_3H_7 (VII-A13) should be considered as isoelectronic. The CH_3 group as depicted in VIII-A13 is, of course, not actually a "CH_3 group" (it was excised for illustrative purposes from the nonbornyl cation); it is a trialkyl CH_2 group and, therefore, more amenable to the five-coordination situation (see Table II).

2. *B_4H_{10} Family of* arachno-*Carboranes*

The parent B_4H_{10} (I-A14) is not a very stable borane (*82*), perhaps due to the four marginal 6′6-bridge hydrogens. For illustrative purposes, if a bridge hydrogen were to be shifted into an endo position (IV-A14), then an even worse situation incorporating a very undesirable $\underline{6'6'}$-bridge hydrogen would be produced.

By contrast, if one bridge proton was removed from B_4H_{10} (I-A14) to produce $B_4H_9^-$, then the two structural choices would be II-A14, related to the parent B_4H_{10} (I-A14), and V-A14. Shore *et al.* (*65*) have carried out an elegant series of experiments showing that the V-A14 structure for $B_4H_9^-$ is preferred at ambient temperatures. Based on hydrogen and boron considerations (rules 2 and 4), the structure V-A14 for $B_4H_9^-$ should have been anticipated as most satisfactory.

Species B_4H_8:LB is known to have structure VI-A14 (*15*, *25*, *77*, *98*) which again should have been expected. The unfavored structure (III-A14) for B_4H_8:LB would have the Lewis base attached to a boron (surrogate carbon) neighboring a bridge hydrogen in an unsatisfactory conflict of interests. The Lewis base in this case would not have the option of migrating to another boron in order to eliminate this structural indiscretion, as was the case in Onak's (*88*, *106*) rearrangement of structure VII- to VI-N6.

A CB_3H_9 compound would be expected to have a VI-A14-type structure.

3. B_5H_{11} *Family of* arachno-*Carboranes*

The structure of B_5H_{11} is apparently I-A15 in the liquid phase (*173*, *174*), although it is reported (*94*) to have a different structure (II-A15) in the crystal phase. The difference in position (i.e., bridge hydrogen vs. endohydrogen) in B_5H_{11} would be indistinguishable between I-A15 and II-A15 and could not be differentiated in the vapor phase by present microwave techniques. In any case, B_5H_{11} is an unstable compound and in the liquid phase structure (I-A15), the two 6′6-bridge hydrogens, although undesirable, are probably less undesirable than would be the overly coordinated BH_2 group (violation of rule 4p) in the crystal phase structure (II-A15). Evidently packing forces favor II-A15 in the latter case.

A large research group at Indiana University (*18*, *80*, *105*, *120*) has obtained splendid line-narrowed ^{11}B NMR spectra which, however, should also favor I-A15. Yet if a continuum of BE hydrogens (especially in the *arachno*-boranes) is simply accepted, then polemics as to whether the bridge hydrogen or endohydrogen structures are correct are of little substance.

When carborane analogs of B_5H_{11} are discovered, it would be expected that an isomer of CB_4H_{10} such as IV-A15 (violating only rule 3s) would be more stable than the isomer III-A15 which contains two undesirable 6′6-bridge hydrogens. Near the completion of this manuscript, Matteson and Mattschei reported (*91*) a CB_4H_{10} isomer for which they suggest the IV-A15 structure.

The Lewis base adduct of B_5H_9 (B_5H_9:LB) may be considered to be isoelectronic with CB_4H_{10} with a LB:B group substituting for the CH group as in IV-A15 or in III-A15. Williams *et al.* (*103*), by contrast, once suggested the structure V-A15 for B_5H_9:LB, which would be isoelectronic with a methylene derivative of B_4H_{10} (I-A14).

In the light of the currently recognized importance of BE hydrogens, a comparison of all three structures (III-, IV-, and V-A15) reveals that the bridge hydrogen environments improve in the order V-A15 (four 6′6-bridge hydrogens), III-A15 (two 6′6- and one 65-bridge hydrogens), to VI-A15 which has three uncompromised 65- and 66-bridge hydrogens.

The V-A15 structure was first suggested for B_5H_9:LB to account for the apex-to-base methyl migration of $1\text{-}CH_3B_5H_8$ in the presence of a Lewis base (i.e., two sets of borons become equivalent in a V-A15 intermediate), but the Lewis base equivalents of IV-A15 or III-A15 would also account for this result. Kodama (*73*) has verified that the rearrangement involves an adduct rather than the ion pair (LB : H^+ and $CH_3B_5H_7^-$).

The IV-A15- or III-A15-type structures for B_5H_9:LB would also be ideal precursors for a di-Lewis base adduct since the structure of $B_5H_9(P(CH_3)_3)_2$ has one of the Lewis base units on the apex (*127*) and one on the base.

4. B_6H_{12} *Family of* arachno-*Carboranes*

The structure of B_6H_{12} is I-A16 (*18*, *82*). The more stable isomer of a possible monocarba derivative (CB_5H_{11}) should have the structure II-A16, with three 66-, 65′- ,and 65-bridge hydrogens rather than the structure of a methylene derivative of B_5H_{11} (I-A15) (e.g., $CH_2B_5H_9$ with the methylene bridging the two BH_2 groups and encompassing four 6′6-, 6′6-, 66-, and 65-bridge hydrogens).

In contrast, Shore *et al.* (*117a*) have shown that the preferred structure of the isoelectronic $B_6H_{11}^-$ is best described as related to B_5H_{11} (I-A15), i.e., μ-$BH_3B_5H_8^-$ with four 65′-, 66-, and 65-bridge hydrogens.

5. B_7H_{13} *Family of* arachno-*Carboranes*

The parent B_7H_{13} might be expected to have a structure resembling a μ-$BH_3B_6H_{10}$ with 76- and 75′- and two 66-bridge hydrogens or, less likely, I-A17. However, B_7H_{13} has never been isolated, perhaps because a BH_3 group could be easily lost to produce the structurally related B_6H_{10} (I-N6). Removal of one proton from μ-$BH_3B_6H_{10}$ could produce μ-$BH_3B_6H_9^-$ (or $B_7H_{12}^-$) with no overly coordinated bridge hydrogens. The II-A17 isomer of CB_6H_{12} should be more stable than its bridge hydrogen tautomer (III-A17) because of bridge hydrogen considerations. Possibly a methylene derivative of B_6H_{12} ($CH_2B_6H_{10}$) should be anticipated.

There is an alternative structural pattern that suggests another configuration for B_7H_{13}: the parent *arachno*-boranes are built up by the monotonic additions of borons in the series $B_3H_8^-$, B_4H_{10}, B_5H_{11}, and B_6H_{12} (I-A13, I-A14, I-A15, and I-A16, respectively) in Figs. 13 through 16.

One additional boron (i.e., one additional triangle) is added in each case after which the two endohydrogens (first) and the bridge hydrogens (second) are placed in lowest possible coordination sites. Such a candidate structure for B_7H_{13} may be easily envisioned and is displayed as IV-A17. Inasmuch as the aforementioned series also becomes progressively less stable with increasing molecular weight, it is anticipated that such a structure as IV-A17 for B_7H_{13} would be extremely unstable.

6. B_8H_{14} *Family of* arachno-*Carboranes*

The parent B_8H_{14} (*22*) is unstable, as might be anticipated from the compromising presence of at least one $\underline{76}'$-bridge hydrogen in either of the possible candidate structures I- or II-A18. The ^{11}B NMR spectrum, reflecting the 4:2:2 kinds of boron, implies rapid tautomerism involving species such as I- and II-A18. An anion, $B_8H_{13}^-$, with the $\underline{76}'$-bridge hydrogen missing from I-A18, should be more stable.

Removal of the least stable or most acidic $76'$-bridge hydrogen from the most favored isomer of B_8H_{14} (I-A18) and the substitution of one of the terminal hydrogens with a Lewis base and one of the bridge hydrogens with a $—(CH_3)_2N—$ group produces the known crystal phase structure for μ-$(CH_3)_2NB_8H_{11}$:LB (III-A18) (*81*, *82*), which violates no rules.

Species B_8H_{12} (III-N8) is stabilized in the presence of ethers; indeed, its ^{11}B NMR spectrum changes dramatically in ether (*22*) revealing adduct formation and, thus, probably an isoelectronic relationship with B_8H_{14} (I-A18). Bridge hydrogen tautomerism plus ether exchange (see IV- and VIII-A18, etc.) probably accounts for the relatively simple ^{11}B NMR spectrum of B_8H_{12} in ether. A static adduct is evidently produced from B_8H_{12} in the presence of CH_3CN, as opposed to $O(C_2H_5)_2$, which probably has the structure VII-A18, compatible with the much more complex ^{11}B NMR spectrum observed (*22*).

Studies are under way to determine the structures of the $C_2B_6H_{10}$ (V-N8 or X-N8) Lewis base adducts, i.e., $C_2B_6H_{10}$:LB. The structural antecedent (V-N8) would favor VI-A18, but V-A18 should be more stable, i.e., satisfying one carbon and one endohydrogen more completely without compromising the 55-bridge hydrogen.

If hydrogen was lost and an additional Lewis base incorporated, i.e., if $C_2B_6H_8$ $(:LB)_2$ was produced, the most stable isomer should have structure IX-A18. It is assumed that the two remaining endohydrogens in IX-A18 would be almost but not quite equally content on either the isoelectronic LB:B or CH groups. However, a residual capacity of boron to accommodate the higher-coordination numbers (Table II) should bias the endohydrogens towards association with the LB:B moieties rather than with the CH groups.

7. B_9H_{15} *Families of* arachno-*Carboranes*

The parent species *i*-B_9H_{15} (I-A19) (*21*) and *n*-B_9H_{15} (XI-A19) (*76*, *125*, *130*) are displayed in Fig. 19. The latter is more stable, probably because it has only two marginally satisfactory 6′6-bridge hydrogens compared to the very unsatisfactory $\underline{76'}$-bridge hydrogen in I-A19. Compound *n*-B_9H_{15} (XI-A19) is known to be capable of ejecting BH_3 groups to form B_8H_{12} (III-N8). No carborane isomers of *n*-B_9H_{15} (XI-A19) are known; a few are suggested such as VII-, VIII-, and XII-A19.

The less stable *i*-B_9H_{15} isomer (I-A19) incorporates at least two (perhaps three) endohydrogens and four (perhaps three) bridge hydrogens as well as one very unfavorable $\underline{76'}$-, one 76-, and two 66-bridge hydrogens; BE hydrogen tautomerism accounts for the ^{11}B NMR spectrum.

One *arachno*-carborane isomer of *i*-B_9H_{15}, namely $C_2B_7H_{13}$, is known; its structure is II-A19 (*136*). The carbons and endohydrogens collaborate in occupying five-coordinate CH_2 sites primarily because the "extra" hydrogens' desire to occupy an endo (terminal hydrogen) site rather than a bridge hydrogen site. This is in contrast to *nido*-carboranes wherein the extra hydrogens were almost always bridge hydrogens, and carbons and bridge hydrogens avoided adjacent structural sites in all cases. It follows that the most stable isomer of *i*-$C_3B_6H_{12}$ should have the structure III-A19.

In these cases, I-, II-, and III-A19, conservation of the 3-center bonds would require five (or six) 3-center bonds to be expressed within the skeleton matched with four (or three) 3-center bridge hydrogens, respectively. There are several examples demonstrating that the nine-vertex arachno system is flexible enough to adapt to both electronic alternatives. The structures for *i*-B_9H_{13}:LB (X-A19) and *i*-$B_9H_{14}^-$ (A-V19) are both known in the encumbered crystalline phases and both must accommodate six 3-center bonds within the skeletal framework. By contrast, *i*-$C_2B_7H_{13}$ (II-A19) absorbs only five 3-center bonds within the skeletal framework.

Others have noted that the encumbered X-ray-determined structures of *i*-$B_9H_{14}^-$ (V-A19) (*43*) and *i*-B_9H_{13}:LB (X-A19) (*82*) both involve two bridge hydrogens and three endohydrogens. However, the relative positions of these five extra hydrogens are not the same in both cases. The differences have been attributed to the presumed influences of charge smoothing and/or resonance stabilization.

Our prejudices favor either crystal packing considerations or, more likely, the fact that X-A19 has fewer desirable locations for bridge hydrogen placement (i.e., locations adjacent to the positively charged LB:BH group are shunned).

In the unencumbered liquid phase, *i*-$B_9H_{14}^-$ should have structure VI-A19 and *i*-CB_8H_{14} should have a similar structure (IX-A19). The conflicting structures for i-$B_9H_{14}^-$ (V- and VI-A19) actually constitute just another case wherein it makes little difference whether the unique hydrogen is endo or bridge; the absolute position of the unique hydrogen in space would be essentially the same (whether it were bridge or endo) and crystal packing forces would have little difficulty in centering the unique hydrogen as an endohydrogen even if it were a bridge hydrogen in the unencumbered fluid phase. This situation parallels the B_5H_{11} case (I- and II-A15) in which it makes little difference whether the reference is to bridge or to endohydrogens. Evidently the V-A19 or VI-A19 structure for i-$B_9H_{14}^-$ is favored over n-$B_9H_{14}^-$ since removal of a proton (probably a 6′6-bridge hydrogen) from n-B_9H_{15} produces i-$B_9H_{14}^-$.

8. [$B_{10}H_{16}$] *Family of* arachno-*Carboranes*

The parent *arachno*-borane $B_{10}H_{16}$ has never been observed (it would have two very undesirable $\underline{76'}$- and two 76-bridge hydrogens); however, the marginally stable derivative $B_{10}H_{15}^-$ has been studied by Rietz *et al.* (*122*) and the data as interpreted by Siedle (*128*) seemingly indicate that the anticipated $B_{10}H_{15}^-$ structure (I-A20) is correct even though it contains one $\underline{76'}$-bridge hydrogen (probably stabilized by the negative charge); tautomerism should be rampant in the liquid phase and no doubt accounts for the ^{11}B NMR data. The formal removal of one bridge hydrogen (as an H^+) from $B_{10}H_{15}^-$ (I-A20) or the addition of two electrons to $B_{10}H_{14}$ (I-N10) produces the very stable $B_{10}H_{14}^{2-}$ (IV-A20) with two rather stable 66-bridge hydrogens (*69*). The structure of $B_{10}H_{12}(:LB)_2$ (III-A20), with which $B_{10}H_{14}^{2-}$ is isoelectronic and isostructural has been accepted for many years (*82*). The most stable structure for $C_2B_8H_{14}$ analog of $B_{10}H_{16}$ should also have the III-A20 structure with CH_2 groups replacing LB:BH group (see also V-25). Stibr *et al.* (*132a*) isolated and identified the most stable isomer of $C_2B_8H_{14}$ (V-25) as well as arachno isomers of $C_2B_8H_{12}^{2-}$.

The Lewis base adduct of the $C_2B_8H_{12}$ isomer (XX-N10) (*38*) has been isolated and should have structure V-A20 ($C_2B_8H_{12}$:LB) which incorporates an undesirable 6′6-bridge hydrogen. By contrast, the Lewis base adduct of the other known isomer of $C_2B_8H_{12}$ (XI- or XVI-N10) (*118*) should have structure VI-A20 ($C_2B_8H_{12}$:LB) and should be more stable due to the uncompromised 66-bridge hydrogen.

9. [$B_{11}H_{17}$] *Family of* arachno-*Carboranes*

Just as the removal of one highest-coordination vertex from the most likely, closo, thirteen-vertex polyhedron (e.g., IV-C4) produces the most probable candidate, namely, nido twelve-vertex polyhedral fragment (see Fig. 12), the removal of one additional high-coordination edge position (adjacent to the open face) should produce the eleven-vertex arachno fragment (marred by a seven-coordinate boron) as typified by I-A21 with a heptagonal open face for occupation by the six extra hydrogens.

No eleven-vertex arachno species is known, but $B_{10}H_{13}^-$ (III- and IV-N10) (*129*, *132*) in the presence of diborane indulges in total boron and hydrogen exchange, and a transient arachno intermediate $B_{11}H_{16}^-$ has been suggested (*124*).

$$B_{10}H_{13}^- + [BH_3] \leftrightharpoons [B_{11}H_{16}^-]$$

The expected configuration for $B_{11}H_{16}^-$ (I-A21) allows both endo-hydrogens to occupy lowest possible coordination sites and allows for satisfactory 66-bridge hydrogen sites; the seven-coordinate boron (violation of rule 4p) is unfavorable, but, in light of the predisposition of seven-coordinate borons to facilitate wholesale valence bond tautomerism (e.g., $B_{11}H_{11}^{2-}$), this feature would account for the complete scrambling of all borons. An alternative and less probable structure for $B_{11}H_{16}^-$ is represented as II-A21, which is produced by breaking one bond in the I-N11 skeletal configuration; a very undesirable $\overline{76'}$-bridge hydrogen would be present (possibly stabilized by the negative charge), but the seven-coordinate boron (violation of 4p) would be avoided.

D. HETEROATOM CARBORANE ANALOGS

There are a number of heteroatoms that can substitute for either boron or carbon in the carboranes. The groups that are as electron-deficient as BH groups are listed vertically to the left of the center line in Table V, whereas those that are as capable as carbon in donating electrons are listed to the right of the center line. The transition elements for the most part electronically substitute for boron and occupy high-coordination sites, but upon electron demand the transition element may also substitute for carbon and concomitantly occupy low-coordination sites. Several transition element moieties, by contrast, are one more electron deficient than boron and occupy, as would be anticipated, high-coordination positions and require additional electron donors (CH groups) to counter the electronic deficit (XIII-24).

In abridged form, we shall discuss in order (*a*) BH-substituted heteroatom carborane analogs (Fig. 22), (*b*) CH-substituted heteroatom carborane analogs (Fig. 23), (*c*) transition element group (TEG)-substi-

TABLE V

ISOELECTRONIC EQUIVALENTS OF VARIOUS GROUPS

		High			Low			
				"BH"	"CH"			
		−3e	−2e	−1e	0	+1e	+2e	+3e
II	a	Be^+	$\mathrm{Be}/\mathrm{BeH}^+$	BeH	$\underline{\mathrm{BeH}^-}$			
					(BeNR_3)			
			Mg/					
	b		Zn/		ZnH^-	$\underline{\mathrm{ZnH}_2{}^{2-}}$		
						$\underline{\mathrm{ZnB}_{10}\mathrm{H}_{12}{}^{2-}}$		
			Cd/		CdH^-	$\underline{\mathrm{CdH}_2{}^{2-}}$		
						$\underline{\mathrm{CdB}_{10}\mathrm{H}_{12}{}^{2-}}$		
						$\underline{\mathrm{HgB}_{10}\mathrm{H}_{12}{}^{2-}}$		
III	a		B^+	B/BH^+	$\underline{\mathrm{BH}}$	BH^-		
						$\mathrm{B}(\mathrm{NR}_3)$		
			Al^+	$\mathrm{Al}/\mathrm{AlH}^+$	$\underline{\mathrm{AlH}}$	AlH^-		
	b		Ga^+	$\mathrm{Ga}/\mathrm{GaH}^+$	$\underline{\mathrm{GaH}}$	GaH^-		
			In^+	$\mathrm{In}/\mathrm{GH}^+$	InH	InH^-		
IV	a			C^+	$\underline{\mathrm{C}}/\mathrm{CH}^+$	$\underline{\mathrm{CH}}$	CH^-	
							(CNR_3)	
				Si^+	Si	$\underline{\mathrm{SiH}}$	SiH^-	
	b			Ge^+	Ge	$\underline{\mathrm{GeH}}$	GeH^-	
				Sn^+	$\underline{\mathrm{Sn}}$	$\underline{\mathrm{SnH}}$	SnH^-	
V	a				N^+	$\underline{\mathrm{N}}$	NH	NH^-
					P^+	$\underline{\mathrm{P}}/\underline{\mathrm{PH}^+}$	PH	PH^-
	b				As^+	$\underline{\mathrm{As}}$	AsH	AsH^-
					Sb^+	$\underline{\mathrm{Sb}}$	SbH	SbH^-
VI	a					S^+	S/SH^+	SH
	b					Se^+	Se	SeH
						Te^+	Te	TeH

tuted carborane analogs (Fig. 24), and (*d*) the coherent interesting consequences that arise in those cases in which the two extra electrons required for stability are donated by one heteroatom, such as S or NH (Fig. 25), rather than carbon.

1. *BH-Substituted Heteroatom Carborane Analogs*

Groups from Table V such as $BeN(CH_3)_3$ (I-22) (*114*), AlR (*92*, *177*) GaC (II-22) (*46*), Sn (III-22) (*146*), and perhaps a bare carbon (IV-22) (*139*) are found substituting isoelectronically for BH groups.

These heteroatom moieties should opt, in the most stable isomers, for the higher-coordination-numbered positions when choices are present.

2. *CH-Substituted Heteroatom Carborane Analogs*

Several groups are known that are evidently isoelectronic with CH groups and as such, when choices exist, preempt lowest-coordination sites.

For example, the Zn, Cd, Ni, and Hg moieties in $M(B_{10}H_{12})_2^{2-}$ (*44*, *47*) substitute for CH groups (or BH^- groups) in two molecules of $B_{11}H_{13}^{2-}$ (IV-N11), and, thus, I-23 becomes isoelectronic with $B_{11}H_{13}^{2-}$ (IV-N11), with Zn occupying an edge site as would a CH group (*71*).

3. *Transition Element Heteroatom Carborane Analogs* (*50*, *155*)

For simplicity, TEG in Fig. 24 stands for transition element group including the transition element atom and attached moieties (e.g., $C_5H_5^-$, $(CO)_n$, and $C_2B_9H_{11}^{2-}$). For the purposes of this discussion the interest is in the transition element atom insofar as it substitutes for BH groups and not in what other flotsam is attached. In general, the transition elements substitute for BH groups and when the coordination number is unusually high (even for boron) the transition element atom preempts the highest position. Thus, in $C_5H_5CoC_2B_8H_{10}$ (I-24) (*52*) and in $C_5H_5CoC_2B_{10}H_{12}$ (II-24) (*17*, *23*, *26*) the transition element atoms are found in the seven-coordinate positions; structure III-24 should be a slightly more stable isomer than II-24 when both the transition atom and carbon are in optimal positions. The second most desirable location for carbon should be the six-coordinate site farthest removed from the seven-coordinate positions if the choice is between six-coordinate sites. Reassuringly, exactly as predicted, the most stable isomer *closo*-TEG-$C_2B_{10}H_{12}$ (III-24) is produced upon heating II-24 [Dustin *et al.* (*26a*)]. These authors also subscribe to the old (*172*) carbon placement considerations (rule 3) but point out the "mysterious" predilection of the TEG and the carbon to become separated in the most stable isomers.

That the initially suggested structure for TEG-$C_2B_{10}H_{12}$ (IV-24) (*53*) has been shown to be incorrect augurs well for the CNPR approach, since IV-24 was based on an illogical thirteen-vertex deltahedron (violation of rule 1p); see IV-C4 for the more reasonable deltahedral alternative.

Many other transition atoms simply substitute for the standard six-coordinate BH groups. Representative examples are in the seven-, eight-, nine- (*45*), ten-, eleven-, and twelve-vertex (*50*) closo species displayed as V-, VI-, VII- VIII-, and I-24 and the group IX-, X-, XI-, and XII-24, which illustrate the diversity possible.

In the icosahedral group of compounds (IX- to XII-24) there are no obviously preferred vertices for carbon occupation and/or transition element occupation, and it is interesting to note that, upon heating one isomer of TEG-$C_2B_9H_{11}$ (IX-24), a number of other isomers are formed (*51*). It would appear that there is no overriding first-order driving force that tends to place carbons adjacent to or apart from the transition atom in the icosahedron. The carbons in such species tend to become nonadjacent upon heating, just as occurs when the parent 1,2-$C_2B_{10}H_{12}$ isomer (II-C3) is treated to produce the 1,7- and 1,12-isomers (II- and III-C2).

There are groups incorporating a transition metal element atom that contribute fewer skeletal electrons than a BH group; these include the $(CO)_3Mn$ unit of $(CO)_3MnC_3B_3H_6$ (XIII-24) (*45*) [to be compared with $C_2B_5H_7$ (V-C2)] and the C_5H_5Fe unit of ferrocene $Fe(C_5H_5)_2$ (XVI-24) [to be compared with $C_4B_2H_6$ (IX-N6)], wherein the transition element occupies the highest-coordination position available (substituting for a boron); but since the transition element contributes one less electron than boron, the inclusion of an additional carbon to make up the difference is necessitated. Alternatively, the iron group in $C_2B_3H_7Fe(CO)_3$ is only as electron deficient as a BH group (*10*) (not shown). Both compounds are isoelectronic with B_6H_{10} (I-N6).

It has been suggested (*27*) that the XIV-24 structure accounts for the various types and abundances of boron in the ^{11}B NMR spectrum (2:2:2:1) of $(CO)_3CoCB_7H_8$. Although XIV-24 may be correct, XVII-24 should have the same numbers of types and abundance ratios and should be more stable, as the carbon would be in the more desirable, low-coordination number position.

More disturbing is the proposed (*68*) structure XV-24 (to account for boron type and abundance in the ^{11}B NMR spectrum) rather than XVIII-24. It is important not to lose sight of the fact that the thermodynamically less stable isomers may frequently be produced during a gentle synthesis; XV-24 and XVIII-24, however, present a striking exception to the thoughts thus far presented in this manuscript. Structure XV-24 is quite possibly correct but it should be much less stable than XVIII-24. In the present author's choice (XV-24), a Co that is isoelectronic (in this case with boron) is found in a lower-coordination edge site (violating rule 4p) while one carbon is found in the highest possible coordination sites (a violation of rule 3p). The preferred XVIII-24 isomer would also have exactly the boron types and abundances required to account for the observed ^{11}B NMR spectrum.

As one illustrative example, since Co is seen to inhabit BH or highest-coordination sites in general, it is noteworthy that a cobalt in its more reduced form (i.e., furnishing an additional electron into the cage) substitutes, in such cases, for a CH group and is, therefore, found, as would be expected, in a low-coordination site (I-23).

E. ONE HETEROATOM DONATING TWO ELECTRONS

In the two series enumerated in the following, it would be expected that the extra electrons would be progressively more difficult to delocalize smoothly: first series—$B_{10}H_{10}^{2-} < CB_9H_{10}^{-} <$ 1,10-$C_2B_8H_{10} <$ 1,6-$C_2B_8H_{10} < B_{10}H_8(LB)_2 < SB_9H_9$; second series—$B_{12}H_{12}^{2-} < CB_{11}H_{12}^{-} <$ 1,12-$C_2B_{10}H_{12} <$ 1,2-$C_2B_{10}H_{12} < SB_{11}H_{11} < (CH_3)_3$-$NCB_{10}H_{10}$. The order may be explained as follows: B_nH_n species are not predicted to be stable; two additional electrons are required and thus $B_nH_n^{2-}$ species are known. For illustrative and bookkeeping purposes these two additional electrons may be defined as "requisite" electrons. In isoelectronic cases such as the closo species ($C_2B_nH_{n+2}$), each carbon donates one of the two requisite electrons.

In the $B_nH_n^{2-}$ species the skeletal electrons and the concomitant negative charges would be as evenly distributed throughout the molecular skeleton as possible. When carbon (or carbons) donate the requisite electrons, the carbons would tend to become positively charged and, thus, tend to distort the donated electrons back toward the carbons. *Thus, the most electron-rich environments are at the same time the most positively charged.*

When the requisite electron that is donated comes from a Lewis base, passes through a boron and on into the skeletal system, then even less complete donation and even more polarization of positive and negative charges should be anticipated. When the two requisite electrons are donated by one heteroelement atom, such as S or NH, the polarization of positive and negative charge should increase substantially over the previous cases. This effect should be maximized in the case where a Lewis base donates electrons to carbon [e.g., the $(CH_3)_3NC$ group in the last example cited] which, in turn, passes the requisite two electrons on into the cage system. In the latter case the carbon donates the two requisite electrons that had been "borrowed" from the Lewis base.

Consider the ten skeletal atom series of thiaboranes in Fig. 25, *closo*-SB_9H_9 (*115*), *nido*-SB_9H_{11}, and *arachno*-$SB_9H_{12}^-$ (*57*). Based on first principles, elucidated in the previous sections and as displayed in Figs. 2, 10, and 20, the sulfur atoms would be placed in the carbon preferred positions as represented by I- and probably II- and III-25, respectively. The presence of bare sulfurs in structures I- and II-25 could be expected. Logically, it would have been expected (incorrectly, as it turns out) that a terminal hydrogen would be placed on the sulfur atom in $SB_9H_{12}^-$ as displayed in III-25. The hypothetical parent of structure III-25 (with one more bridge hydrogen) is represented as VII-25.

Refocusing attention on $SB_9H_{12}^-$ (III-25), the sulfur atom, doing the job of two carbons (i.e., contributing two electrons into the boron skeletal framework), should become much more positively charged than would be a carbon in a comparable situation. Structure III-25 should then be highly polar with a positive charge on sulfur and a negative charge distributed among the borons. This polarization in $SB_9H_{12}^-$ (III-25), if unsatisfactory, could be alleviated in at least three ways, e.g., the migration of a positively charged proton from the sulfur onto the cage to produce the zwitterion tautomer VI-25 or, alternatively, by placing the sulfur in alien, more highly coordinated positions as displayed in structure IV- or VIII-25. The proton migration to produce the zwitterion [dipolar ion or inner salt; $SB_{12}H_{12}^-$ (VI-25)] is completely compatible with the ^{11}B NMR spectrum, and the absence of an SH group in the ^1H NMR spectrum demonstrates that the author's choice (*57*) of VI-25, as the structure for $SB_9H_{12}^-$, is correct (*128*).

Two effects become apparent in the above cases and they should work in opposition: electron-sufficient carbon donates electrons into the skeletal framework but (*a*) wants and frequently gets the least alien, lowest available coordination site (rule 3) [see, for example, 2,4-$C_2B_5H_7$ (V-C2)]; alternatively (*b*), could not the carbons more efficiently donate their extra skeletal electrons if they were in the most highly coordinate apex sites of the pentagonal bipyramid (i.e., a *closo*-1,7-$C_2B_5H_7$)? Although effect (*a*) seems most important in the case of carbon, it may not be in the case of sulfur which accounts for the inclusion here of candidate structures IV- or VIII-25 for $SB_9H_{12}^-$ for illustrative purposes, even though they are known to be incorrect for the structures thus far discovered. Perhaps effect (*b*) will be found to be the dominant theme in some subsequent investigations.

Although the suggested rearrangement to produce the zwitterion is a satisfying way to visualize the preference of structure VI-25 over III-25 in the case of $SB_9H_{12}^-$, in actuality the sulfur attached proton in the hypothetical parent SB_9H_{13} (VII-25) can simply be recognized as most acidic, and, therefore, the anion VI-25 would simply be derived from the parent VII-25 by the removal of that sulfur-attached proton.

This rationalization of the data, with an extreme case of charge smoothing as the driving force, is made more believable as a result of Shore's (*63*) placement of a proton in the one available vacancy about the base of B_6H_{10} (I-N6) to produce $B_6H_{11}^+$ which has no such driving force [a compound predicted to be stable by Lipscomb (*82*)].

If one accepts the explanation for the correctness of structures VI-25 and XIII-25 as based on dipolarization considerations due to the necessity of S and N to donate two electrons, would there not be at least a similar, smaller but noticeable effect in the case of carbon analogs wherein each carbon donates only one electron into the cage?

Only one example has been published [i.e., $C_2B_7H_{13}$ (II-A19)] and it confirms these suspicions (*136*). The two bridge hydrogens and the two endohydrogens of the CH_2 groups in $C_2B_7H_{13}$ are acidic, and although all four hydrogens exchange to produce $C_2B_7H_9D_4$ when $C_2B_7H_{13}$ (II-A19) is mixed with excess D_2O and K_2CO_3, the salt Cs^+ $C_2B_7H_{12}^-$, upon neutralization by DCl, produces $C_2B_7H_{12}D$, with the deuterium on the carbon. This reveals that the endohydrogens of the CH_2 groups are more acidic than the bridge hydrogens and that the unencumbered fluid phase structure of $C_2B_7H_{12}^-$ should be that of $C_2B_7H_{13}$ (II-A19) minus an endohydrogen from one of the two CH_2 groups.

Thus, within the arachno species, the endohydrogens of BH_2, CH_2, and $NH_2(SH)$ groups are progressively more acidic; the latter three are more acidic than most two-coordinate bridge hydrogens.

When the *arachno*-carborane $C_2B_8H_{14}$ (V-25) is eventually discovered its anion $C_2B_8H_{13}^-$ should have structure IX-25 rather than X-25 structure based on the greater acidity of an endohydrogen attached to carbon as compared to a bridge hydrogen; stated another way, the zwitterionic configuration (IX-25) will be preferred.* Were it possible to produce $B_{10}H_{11}(:LB)_2^-$ from $B_{10}H_{12}(:LB)_2$ (III-A20), it should be isoelectronic with $C_2B_8H_{13}^-$ (IX-25).

Before leaving structures II-, III-, and IV-25, although III-25 is unstable with respect to VI-25 for an isomer of $SB_9H_{12}^-$, there is reason to suspect that the IV-25 isomer of $SB_9H_{12}^-$ may one day be discovered unless sulfur (as compared to carbon) has a greater predilection than carbon for low-coordination sites (which has not yet been ascertained). This suggests that the known *nido*-SB_9H_{11} (II-25) should be reconsidered.

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* Recently, Plesek and Hermanek (*113b*) compiled a review that includes their research and "the intermediate dicarba-*nido*-boranes"; many other new compounds are revealed. Stibr *et al.* (*132a*) had previously isolated the most stable isomer of $C_2C_8H_{14}$ (V-25).

An alternative *nido*-SB_9H_{11} (not shown) would place the sulfur in the higher-coordinate five position (as in IV-25) but result in a more ideal placement of the bridge hydrogens (i.e., two 65-bridge hydrogens as opposed to one 66- and one 65-bridge hydrogen in II-25).

Returning to Fig. 25 and focusing on the hypothetical parent compound SB_9H_{13} (VII-25) that contains two 66-bridge hydrogens, one may ask: Would not that compound also tend to transfer its sulfur-attached proton onto a boron–boron bond to form a zwitterionic tautomer (XI-25) resembling $B_{10}H_{15}^-$ (I-A20) (*122*)? Since 76′- and 76-bridge hydrogens are present in XI-25, the tendency to lose that very acidic bridge proton from XI-25 to become the anion should be considerable. Thus both VII-25 or its tautomeric isomer (XI-25) should be very acidic. In seeming confirmation of this supposition, it has been impossible to date to add a proton to $SB_9H_{12}^-$ (VI-25) to produce either the parent SB_9H_{13} (VII-25) or its zwitterionic counterpart XI-25. Indeed (*57*), compound $H_3O^+SB_9H_{12}^-$ is as strong an acid as $(H_3O^+)_2B_{12}H_{12}^{2-}$ or sulfuric acid for that matter. Perhaps the parent SB_9H_{13} (VII- or XI-25) could be produced from $SB_9H_{12}^-$ (VI-25) in superacid, liquid HI, or in Shore's HCl plus BCl_3 mixture (*127*):

$$SB_9H_{12}^- + BCl_3 + HCl \rightarrow SB_9H_{13} + BCl_4^-$$

Rudolph's SB_9H_9 (I-25) (*115*), where S substitutes for two CH groups, is stable (no extra hydrogens complicate matters); but would not the terminal NH hydrogen in an isoelectronic analog such as NB_9H_{10} be very acidic? Such a compound when synthesized should tend to lose the acidic NH to form $NB_9H_9^-$. A question remains. In the event that this latter anion could be protonated via Shore's techniques or in liquid HI or in superacid (carefully), would the proton locate terminally upon the nitrogen or over a triangular face reminiscent of VIII-C4?

IV. Bridge and Endohydrogens and Relative Lowry-Brønsted Acidity

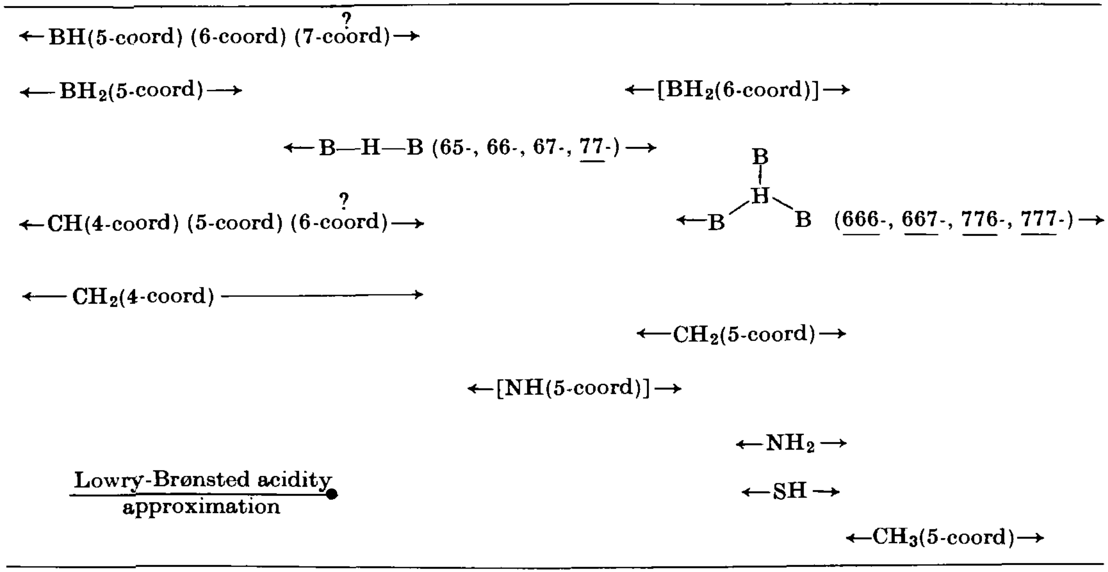
In its current form, CNPR theory has resulted from the recognition that the second most important consideration (rule 2) within carborane structures is the coordination numbers involving the BE hydrogens.

The relative Lowry-Brønsted acidities of the various groups within the carboranes and related species are tentatively listed in Table VI. Further experiments to determine the equilibrium positions involving species such as

$$SB_9H_{12}^- + B_{10}H_{11}^- \rightleftharpoons SB_9H_{13} + B_{10}H_{10}^{2-}$$

TABLE VI

Tentatively Suggested Proton Acidity of Various Groups as a Function of Coordination Number



may reveal relative SH and B_3H (protonated face) acidities complicated by the presence of negative charges.

There are, of course, several kinds of BH and CH groups. Depending on the coordination numbers of the borons and carbons involved, some are more acidic than others. The most interesting acidity order that can now be tentatively handled involves the B_2H (protonated edge) group or the 3-center bridge hydrogens which have been shown [as predicted by Parry and Edwards (*110*)] to differ in degree, i.e., to be more acidic when larger electron-deficient sinks are involved. Hermanek, and co-workers have added the fused *nido*-boranes (*56*, *113c*). In the order of increasing acidity are $B_5H_9 < B_6H_{10} < B_{10}H_{14}$ (*8*, *64*, *66*) $< B_{16}H_{20} < B_{18}H_{22}$ (isomers).

Shore has pointed out that in acidity B_4H_{10} (I-A14) (*65*) lies between $B_{10}H_{14}$ (I-N10) and B_6H_{10} (I-N6). When the various "kinds" of bridge hydrogens are considered, as well as the degree within which they differ, then B_4H_{10} is not an anomalous example. Within the series $B_{18}H_{22}$, $B_{16}H_{20}$, $B_{10}H_{14}$, B_6H_{10}, and B_5H_9 the most highly coordinated bridge hydrogens (and thus the most acidic) are what have been described above as relatively content 66-bridge hydrogens. By contrast, much less content 6′6-bridge hydrogens are present in B_4H_{10}.

When one takes into account then, both the largeness of the electron-deficient delocalized electron sink (*56*, *110*, *113c*) (degree) and the larger effect of the kind of bridge hydrogen (see underlined species in Table VII), then B_4H_{10} falls into line with $B_{18}H_{22}$, $B_{16}H_{20}$, $B_{10}H_{14}$, B_6H_{10}, and B_5H_9. Many other bits and pieces of information also seem to fit.

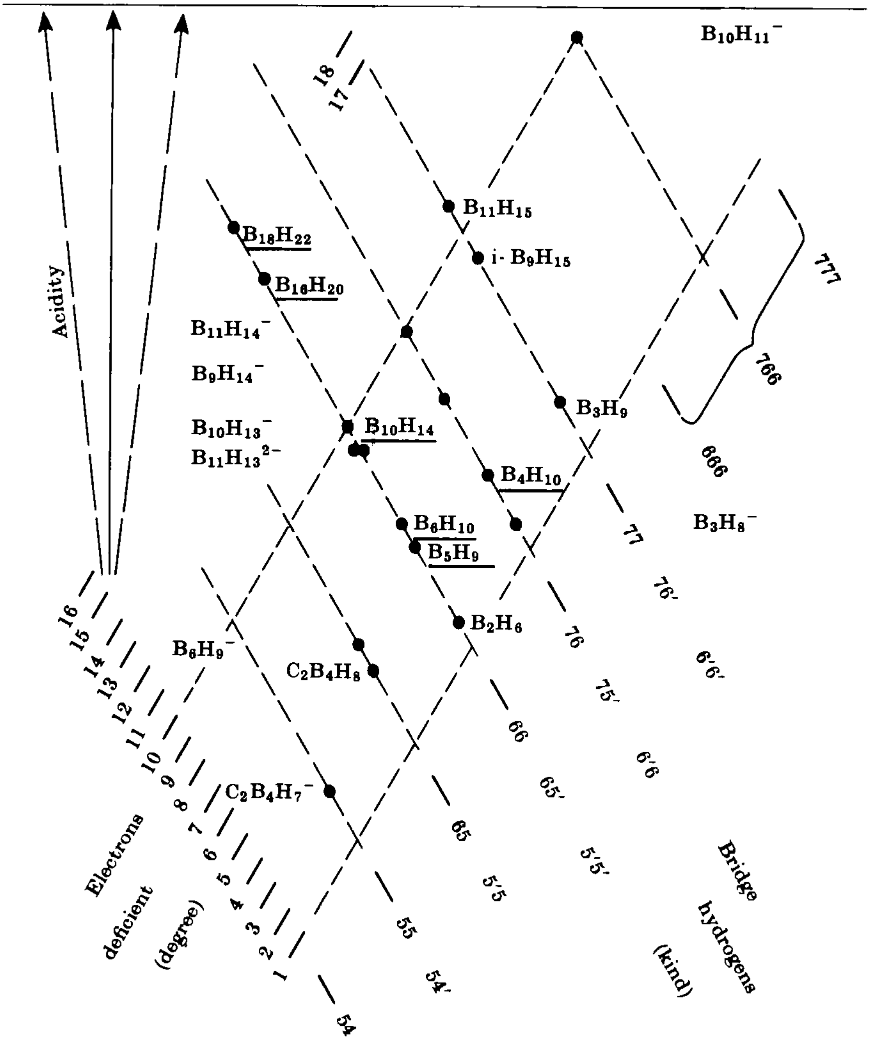
Shore *et al.* (*12*) have confirmed that the presence of electron-withdrawing groups (i.e., ClB_5H_8) promote greater bridge hydrogen acidity, whereas the presence of electron-donating groups (i.e., $CH_3B_5H_8$) lessen bridge hydrogen acidity when compared to the parent B_5H_9. Bridge hydrogen locations are also influenced by such groups (e.g., as in $CH_3B_6H_9$ and BrB_6H_9) (*11*).

In Table VII are illustrated, in greatly oversimplified fashion, the relationships of the known boranes and some carboranes. The lack of acidity of B_2H_6 (*8*) may be attributed to both its small size and 5′5′-bridge hydrogens.

Why is $C_2B_4H_8$ (III-N6) so much more acidic than $C_2B_4H_7^-$ (VIII-N6) and less acidic than B_6H_{10} (I-N6) although all three species are isoelectronic? The B_6H_{10} has a 66-bridge hydrogen to lose and is six electrons deficient, whereas the isoelectronic $C_2B_4H_8$ is only four electrons deficient and has a less acidic 65-bridge hydrogen to lose. Moreover, once $C_2B_4H_7^-$ is formed, only a 55-bridge hydrogen remains, and it is only three electrons deficient and negatively charged besides! These

TABLE VII

OVERSIMPLIFIED LOWRY-BRØNSTED ACIDITY AS A FUNCTION OF "KIND AND DEGREE" OF VARIOUS BRIDGE HYDROGENS



observations give rise to the question: Could bridge hydrogen acidities be utilized as a tool to infer structure?

Why are the *i*-$B_9H_{14}^-$ (VI-A19) and $B_{11}H_{14}^-$ (III-N11) anions stable, but their parents *i*-B_9H_{15} (I-A19) and $B_{11}H_{15}$ (I-N11) are unstable?

The latter have $\underline{76'}$- and $\underline{77}$-bridge hydrogens and are more electron-deficient (see Table VII); it is also reasonable to suggest here that the stability of any of the overly coordinated bridge hydrogens in the anions is greatly enhanced by the presence of the negative charge. Many problems suggest themselves for investigation; among the various atoms within the carboranes, the multivalent hydrogens are evidently the most sensitive to coordination number environment.

In Table VII it has been assumed for illustrative purposes that both differences in degree and kind are linearly related, that the members of the various groups (e.g., $\underline{6'6'}$-, $\underline{76'}$- and $\underline{77}$-) are equal, that many other isoelectronic differences such as the presence of carbons as opposed to negative charges play no role, and that the total number of bridge hydrogens is not relevant, etc. Of course, these assumptions are only partially correct; for example, the presence of negative charge, although extremely important, is neglected (e.g., a 65-bridge hydrogen $B_6H_9^-$ would be much less acidic than a 65-bridge hydrogen on the isoelectronic $C_2B_4H_8$). Of course, B_5H_8–B_5H_8 should be considered as a B_5H_9 derivative, not a 10-boron compound in Table VII.

When more data are accumulated, the various borane anions, carboranes, and neutral boranes should only be compared with each other, rather than all together as in Table VII.

V. Conclusions

There are a number of additional points of view (*29*, *30*, *54*, *87*, *112*, *143*) which the discerning reader will wish to consider; some are complementary, some compatible, some competitive, and some present alternatives to the CNPR theory.

On the preceding pages there has been an attempt to present carborane structural chemistry as clear and orderly. In fact, however, many bits of information are missing, perhaps have been misplaced, or misinterpreted; additional research is needed to fill in the blanks and to correct the errors.

The discriminating reader will note, for instance, that only the neighboring atoms are considered in the assignment of coordination numbers to the carbons (rule 3) and the borons (rule 4). The identities (whether hydrogen, carbon, or boron, etc.) of the neighboring atoms have been neglected. The elements that were "bonded" to the borons involved in the bridge hydrogen count (rule 2) have also been neglected. Advances in CNPR theory may be anticipated when these second-order coordination number considerations are appraised.

For a more general overview, based in part on CNPR theory, which encompasses not only electron-deficient carboranes but also includes metal hydrocarbon π-complexes, cluster and ring compounds, see the preceding article in the present volume, by K. Wade.

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