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Empirical and ab Initio Energy/Architectural Patterns for 73 *nido*-6⟨V⟩-Carborane Isomers, from $B_6H_9^-$ to $C_4B_2H_6$[#]

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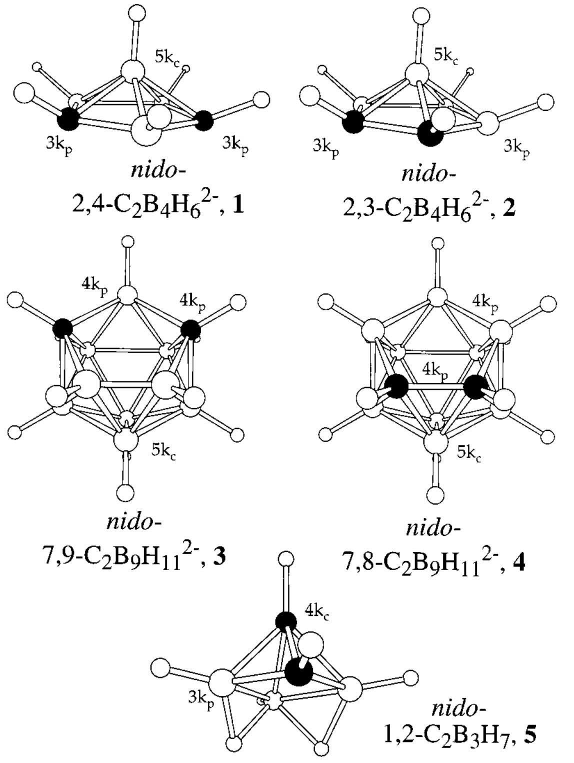
Qualitative rules governing carbon and bridge-hydrogen placement permit the prediction of the most stable isomeric structures for the various carboranes. Seventy-three isomeric boron hydride and carborane structures, from $B_6H_9^-$ to $C_4B_2H_6$, were computed at the ab initio MP2(fc)/6-31G* level to determine their relative stabilities *quantitatively*. Specific architectural features, recognized to be unfavorable, were assigned "energy penalty" values that allow the projection of comprehensive thermodynamic stability values via a simple additivity procedure. These values match the ab initio results with surprising precision. Our study includes Siebert's *nido*-2,3,5-$C_3B_3H_7$ and Wrackmeyer's *nido*-2,4-$C_2B_4H_8$ *nido*-6⟨V⟩ carboranes, which contain "unusual" CH−B-bridge hydrogens.

1. Introduction

The search for hybrids of boron hydrides and hydrocarbons as part of the hunt for high-energy fuels during the early to middle 1950s led to the discovery of compounds labeled carboranes.[1] There are three main classes: *closo*-, *nido*-, and *arachno*-carboranes, which correspond to the molecular formulas; *closo*-$C_{0-2}B_nH_{n+2}$, *nido*-$C_{0-4}B_nH_{n+4}$, and *arachno*-$C_{0-6}B_nH_{n+6}$. They involve $n + 1$ (n equals the number of borons and carbons), $n + 2$, and $n + 3$ skeletal electron pairs, respectively. The structures of the *nido*- and *arachno*-carboranes are constructed by sequentially leaving unoccupied one and two vertexes, respectively, from the various *closo*-deltahedra, the most spherical polyhedra composed exclusively of trigonal faces. The missing vertexes produce deltahedral fragments with four, five, or six-membered open faces. The open faces are identified by Roman numerals; e.g., compounds **1** and **2** in Figure 1 have *nido*-6⟨V⟩ structures. The increasing number of skeletal electron pairs and the larger open faces provide locations for additional skeletal hydrogens (both endo-bridge hydrogens and endo-terminal hydrogens).



nido-2,4-$C_2B_4H_6^{2-}$, **1**

nido-2,3-$C_2B_4H_6^{2-}$, **2**

nido-7,9-$C_2B_9H_{11}^{2-}$, **3**

nido-7,8-$C_2B_9H_{11}^{2-}$, **4**

nido-1,2-$C_2B_3H_7$, **5**

Figure 1. *nido*-2,4-$C_2B_4H_6^{2-}$, **1**; *nido*-2,3-$C_2B_4H_6^{2-}$, **2**; *nido*-7,9-$C_2B_9H_{11}^{2-}$, **3**; *nido*-7,8-$C_2B_9H_{11}^{2-}$, **4**, and *nido*-1,2-$C_2B_3H_7$, **5**.

Among the more recently discovered carboranes are Siebert's *nido*-2,3,5-$C_3B_3H_7$[2] and Wrackmeyer's *nido*-2,4-$C_2B_4H_8$[3] whose structural idiosyncrasies[4] stimulated the following investigation of 73 related compounds with similar configurations. Our

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[#] Dedicated to Professor Jaromir Plesek on the occasion of his 70th birthday. This work was carried out in part at the Institut für Organische Chemie der Universität Erlangen-Nürnberg.

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original goal was to establish a set of empirical rules governing the relative energies of the various isomeric arrangements in as quantitative a fashion as possible. This approach has a distant kinship to Benson's rules[5] wherein the thermodynamic stability of isomeric hydrocarbons can be estimated. The various moieties (e.g., $-CH_3$, $-CH_2-$, $-CH{=}CH-$, etc.) present in a specific structure possess incremental values that can be summed up to give a total heat of formation. Good additivity is found for classical molecules like hydrocarbons. Unlike hydrocarbons, more than two or three isomers of a given carborane composition can seldom be isolated because barriers to rearrangement are quite low. Many synthetic methods produce only one most stable carborane isomer. Moreover, nonclassical compounds like carboranes are characterized by delocalized bonding that might not be expected to behave in an additive fashion.

Our approach to an increment system for assessing relative thermodynamic stabilities does not rely on a summation of "*advantageous*" increments for all moieties to yield a heat of formation[5] for a given structure. Instead, a preponderance of the architectural features are identified and assigned various "energy penalty" values. Thus, in contrast, the sums of these various "*disadvantageous*" energy penalty values (ignoring all zero-impact features) allow the relative thermodynamic stabilities of the various isomers to be estimated and compared to the values by the most recent calculational studies, which are of greater sophistication and precision.[6]

1.1. Carbon Placement Patterns within *closo*-Carborane Configurations. All *closo*-carboranes have their borons and carbons disposed about the vertexes of a specific, unique series of deltahedra[7,8] that incorporate the most homogeneous possible cage (designated with subscript C) vertexes ("inner-sphere" skeletal atoms). Deltahedra are polyhedra that have triangular facets only, and the *closo*-deltahedra of interest here have the most spherical configurations possible. The boron and carbon atoms occupy the deltahedral vertexes, which are usually connected (k) to four or five other heavy skeletal atoms (identified as $4k_C$ or $5k_C$ vertexes). Rarely, $3k_C$ or $6k_C$ vertexes are encountered. Additional exo-terminal groups are not counted in these shorthand designations. Hence, the $4k_C$ and $5k_C$ boron and carbon atoms have total coordination numbers of 5 and 6, respectively.

The preferred vertexes for carbon atom location can be predicted correctly by applying two empirical rules.[9,10] In the order of decreasing significance, these rules are the following: (A) The carbon atoms in the thermodynamically most stable isomers are located at the sites (vertexes) of lowest connectivity. (B) If otherwise equivalently connected sites are available, the carbons will occupy nonadjacent vertexes in the thermodynamically most stable isomers. Deplorably, the postulated specious existence of derivatives of *closo*-1,2-$C_2B_3H_5$ and *closo*-$C_3B_5H_7$[11−13] compromised the acceptance of the generality of rules A and B by most theoreticians and reviewers.

Fortunately, 3 decades later, these two exceptions have been rectified.[14,15] The two empirical patterns, rules A and B, have been supported at higher levels of theory; thus, rules A and B may now be invoked without criticism.

1.2. Carbon Placement Patterns within "Homogeneous" *nido*-Structures. The structural systematics are somewhat more complicated among the nine families of *nido*-carboranes with $n = 4-12$ skeletal boron and carbon atoms.[8] In addition to cage vertexes (k_C) of variable connectivity, e.g., $5k_C$ and $4k_C$, there are also peripheral vertexes (k_P) of variable connectivity, e.g., $2k_P$, $3k_P$, $4k_P$, and $5k_P$ (see Figure 1).

Fortunately, three of the nine families of *nido*-carboranes, i.e., those with 5, 6, and 11 vertexes, have only *one kind of cage* and *one kind of peripheral vertex*. These include the *nido*-5⟨IV⟩ family with *one* $4k_C$ and *four* $3k_P$ vertexes ($\Delta k = 1$), the *nido*-6⟨V⟩ family with *one* $5k_C$ and *five* $3k_P$ vertexes ($\Delta k = 2$), and the *nido*-11⟨V⟩ family with *six* $5k_C$ and *five* $4k_P$ vertexes ($\Delta k = 1$).[16] The carbon-placement rules A and B apply to *nido*-carboranes also but are followed rigorously only when skeletal hydrogens are absent. The placement of both skeletal bridge hydrogens and skeletal endo-terminal-hydrogens are of greater influence than the carbon locations.

For example, *nido*-2,3-$C_2B_4H_6^{2-}$, **2**[17] (which obeys rule A but not B), is known to be less stable than *nido*-2,4-$C_2B_4H_6^{2-}$, **1**,[18] which conforms to rules A and B. Similarly, of the two *nido*-11⟨V⟩ species, *nido*-7,8-$C_2B_9H_{11}^{2-}$, **4**,[19] has recently been calculated to be 16 kcal mol^{-1} less stable than *nido*-7,9-$C_2B_9H_{11}^{2-}$, **3**,[20] as expected. Note that these four carboranes **1**−**4** are restricted to *nido*-6⟨V⟩ and *nido*-11⟨V⟩ skeletons of boron and carbon, with homogeneous peripheral and cage vertexes, and there are no endo-bridge hydrogens or endo-terminal hydrogens present. The empirical rules A and B were shown to predict the correct order of stabilities among all seven of the most probable isomers of *nido*-$C_4B_7H_{11}$ and to rectify the inaccurate structures previously assigned to the second and third most stable isomers of *nido*-$C_4B_7H_{11}$.[16]

1.3. Carbon Placement Patterns Are (Usually) Secondary to Hydrogen Placement Patterns. In *nido*-1,2-$C_2B_3H_7$, **5**[21,22] (Figure 1), one carbon is found in the apex $4k_C$ site rather than

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[6] See also an EHMO study of the $B_6H_9^-$ to $C_4B_2H_6$ isomers: Gill, W. R.; Jones, M. E.; Wade, K.; Porterfield, W. W.; Wong, E. H. *J. Mol. Struct.: THEOCHEM* **1992**, *261*, 161−174. The order of isomer stabilities was frequently correct in the EHMO study. A number of the most stable isomers were not considered, and some proposed isomers were not calculated to be stable species, intermediates, or transition states in our current investigation. See review chapters by Schleyer, P. v. R., Najafian, K., and McKee, M. L. in ref 8.

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in one of the four $3k_P$ locations about the base in contravention to pattern A (the Δk value from base to apex is 1).[1] This preference was attributed to the overriding requirement of the *two* bridge hydrogens to have access to the relatively electron-rich $3k_P$ locations at the expense of *one* carbon being located in a less desirable $4k_C$ site. Could *one* bridge hydrogen atom ever cause one carbon atom to relocate? Could *two* or *three* carbon atoms cause *one* bridge hydrogen to accept a less desirable environment? This study tries to answer such questions by quantifying such structural "conflicts". Energy penalties are introduced for each architectural feature recognized as less than favorable. Carbon atom placements as well as skeletal hydrogen architectural features (endo-bridge-hydrogens and endo-terminal-hydrogens) are evaluated as a function of their class, coordination numbers, connectivities, and electronic charge.[23] The ab initio computed relative energies of not only the 14 *known* structures but also the 59 *hypothetical* structures that are currently *unknown* (some may never be known) allow us to test the validity of the assumed additive behavior of the various architectural features.[23]

Inherently, the electron-hungry skeletal hydrogens (both endo-bridge and endo-terminal) tend to be associated with the more electron-rich boron atoms, i.e., those of (a) the lowest coordination numbers, $4 > 5 \gg 6 \ggg 7$, and (b) the lowest skeletal connectivity, $2k > 3k \gg 4k >>> 5k$. Skeletal hydrogens are predominantly associated with (c) the most electron-abundant class possible, which decreases in the order *hypho* > *arachno* > *nido* > *closo*, and (d) the most electron-rich ionic state, dianion > monoanion > neutral > cation.

Since sophisticated computations are increasingly accurate, why would a simple energy increment system of architectural features be of interest? Chemists are interested not only in the *precise* relative energies but also *why* the structural features resulted in the relative energies. This paper presents a surprisingly accurate rationalization of the relative energies of 72 of the 73 known and unknown members of the *nido*-$B_6H_9^-$–$C_4B_2H_6$ continuum, including many cases where the carbon location and skeletal hydrogen location patterns are in conflict.

A referee points out that "From the work of Hoffmann and Lipscomb onward, there have been many calculational studies of progressively greater sophistication and precision...". Examples would include the work of Wade, Porterfield, McKee, Schleyer, Hofmann, Najafian (and others) who have contributed to the understanding of quantitative relationships within and among borane and carborane systems.[6]

2. Computational Details

All geometries were fully optimized within the given symmetry point group at the MP2(fc)/6-31G* level of theory using the Gaussian 94 program.[4,24,25] The nature of the stationary points were determined by analytical frequency calculations at the HF/6-31G* level.

The empirical energy penalty values in Table 1 and Figure 2 were originally ranked intuitively and refined iteratively by trial and error methods to agree with the calculated ab initio values, resulting in a standard deviation of 3.1 kcal mol^{-1}. The energy penalty values were finally fitted by a statistical program to give the best possible overall agreement with the MP2 relative energies. This procedure reduced the standard deviation to 2.6 kcal mol^{-1}. When rounded off to integers

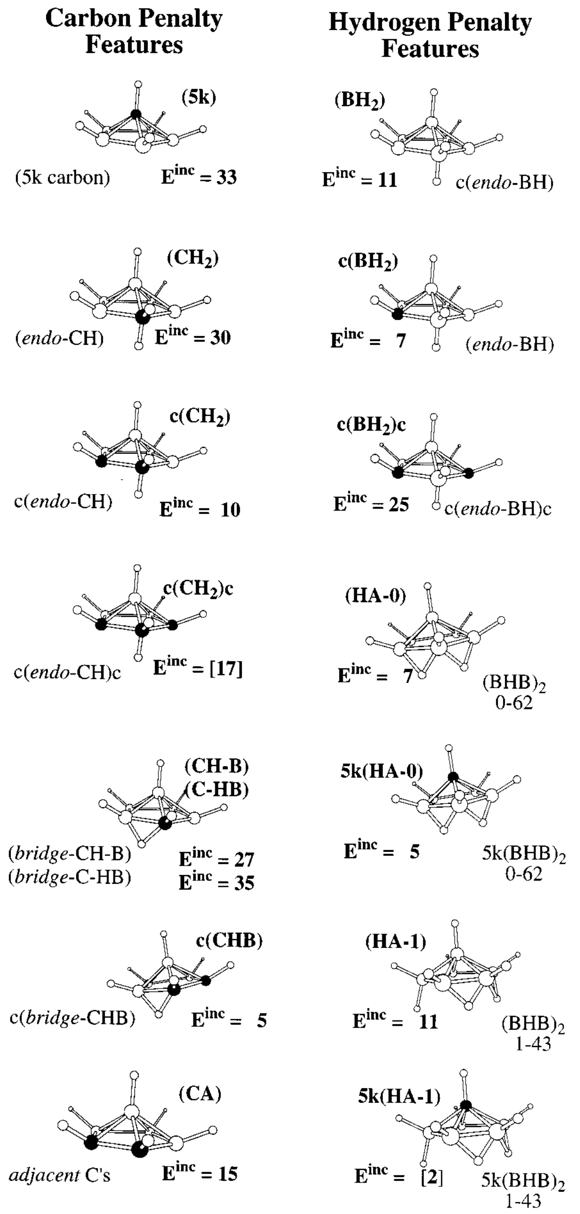

Figure 2. Illustrations of features, symbols, and energy penalties, E^{inc} (in kcal mol^{-1}).

Table 1. Architectural Features and Symbols (Illustrated in Figure 2) and Energy Penalties (in kcal mol^{-1})

features	symbols	energy penalties
5k carbon	5k	33
endo-CH	CH_2	30
c(*endo*-CH)	c(CH_2)	10
c(*endo*-CH)c	c(CH_2)c	[17]
bridge-CH–B	CH–B	27
bridge-C–HB	C–HB	35
c(bridge-CHB)	c(CHB)	5
adjacent carbons	CA	15
endo-BH	BH_2	11
c(*endo*-BH)	c(BH_2)	7
c(*endo*-BH)c	c(BH_2)c	25
$(BHB)_2(0-62)$	HA–0	7
$5k_C(BHB)_2(0-62)$	5k(HA–0)	5
$(BHB)_2(1-43)$	HA–1	11
$5k_C(BHB)_2(1-43)$	5k(HA–1)	[2]

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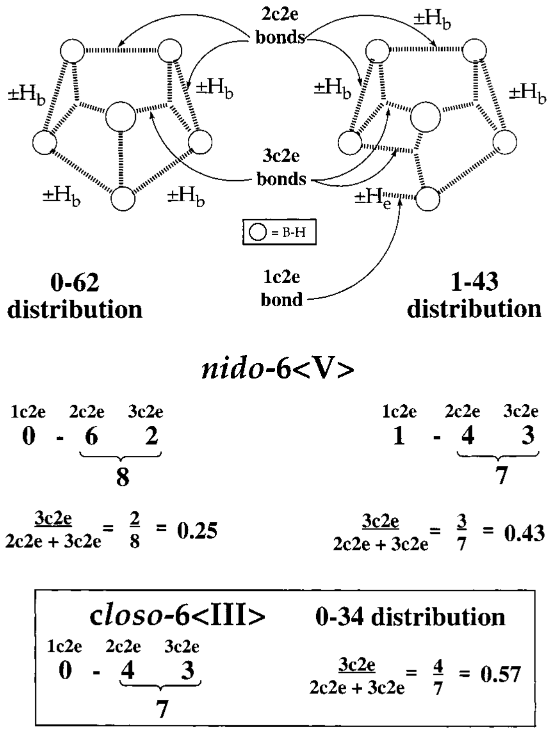
Scheme 1. *nido*-6⟨V⟩ Distributions for Comparison with *closo*-6⟨III⟩



only six of the 15 energy penalty values changed, none by more than 2 kcal mol^{-1}.

3. Results and Discussion

The architectural features, which have been intuitively identified in the past to be associated with lessened thermodynamic stability, are listed in Table 1 and discussed in detail in the following paragraphs. Each of these features is assigned an energy penalty value E^{inc}. For each isomer of interest the penalty values of all structural features present are summed to give $E_{\mathrm{sum}}{}^{\mathrm{inc}}$. Relative energies $E_{\mathrm{rel}}{}^{\mathrm{inc}}$ can subsequently be estimated as differences in $E_{\mathrm{sum}}{}^{\mathrm{inc}}$. Here, the $E_{\mathrm{rel}}{}^{\mathrm{inc}}$ values are referenced to the isomer with the smallest $E_{\mathrm{sum}}{}^{\mathrm{inc}}$ (i.e., the most stable structure). Examples of the various features, their symbols, and energy penalties are illustrated in Figure 2.

How these energy penalty values are applied to the 73 isomers, **AA** to **KH**, will be illustrated in sections 3.3.1−3.3.11 and in Figures 3−13. In just 4 of 70 structures do the empirical $E_{\mathrm{rel}}{}^{\mathrm{inc}}$ and theoretical $E_{\mathrm{rel}}{}^{\mathrm{MP2}}$ values differ by 5 kcal mol^{-1} or more; these structures are **HD**, **IB**, **JG**, and **KG**. Only in isomer **IB** does the difference exceed 7 kcal mol^{-1}. The remaining compounds **CH**, **HG**, and **FD** have unique structural features and are thus inconclusive. From the good agreement achieved we conclude that all the architectural features associated with energy penalties of >4 kcal mol^{-1} have been identified. Part a and b of Table 2 (available in the Supporting Information) relate the prevalence of the various energy penalty values in structures **AA** to **KH** and the differences between the empirical $E_{\mathrm{rel}}{}^{\mathrm{inc}}$ and theoretical $E_{\mathrm{rel}}{}^{\mathrm{MP2}}$ values.

3.1. Penalties Associated with Disfavored Features Involving Carbon. The top eight entries in Table 1 refer to energy penalties involving carbon. A carbon in the apex 5k position (5k) of the pentagonal pyramid results in an energy penalty of 33 kcal mol^{-1}. An *endo*-CH in a CH_2 group (CH_2) imposes a 30 kcal mol^{-1} penalty. If the CH_2 group is adjacent to one carbon, c(CH_2), or two carbons, c(CH_2)c, additional secondary penalties of 10 or [17] kcal mol^{-1}, respectively, are included. Brackets are used to mark provisional values when there is only one example for a particular architectural feature. There are two kinds of CHB bridge hydrogens. The first “more stable” type is the CH−B bridge hydrogen, (CH−B) characteristic of *intermediates* wherein the hydrogen is closer to the carbon than to the boron; an energy penalty of 27 kcal mol^{-1} is imposed. The second “less stable” type is the C−HB bridge hydrogen (C−HB) characteristic of *transition states* wherein the hydrogen

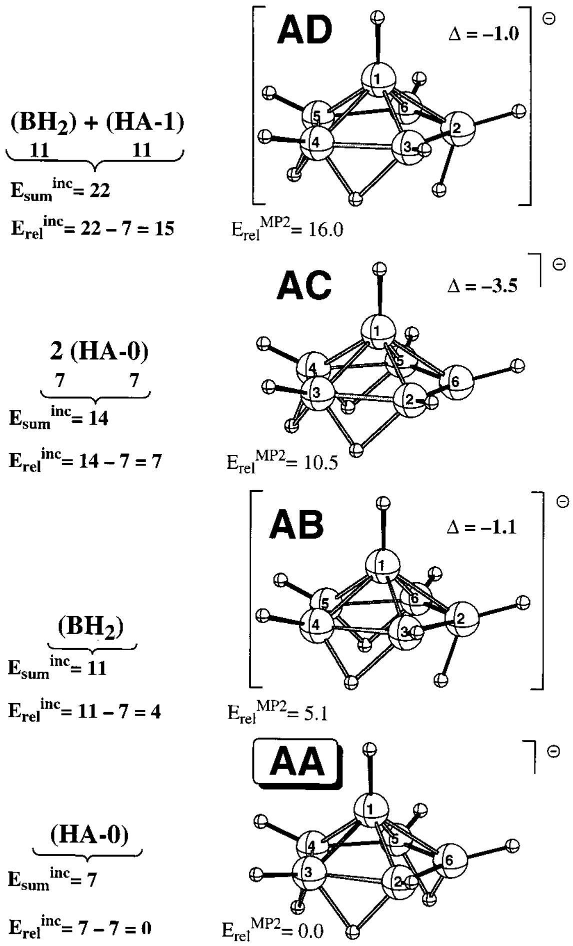


Figure 3. Isomers of *nido*-$B_6H_9{}^{1-}$, **AA** to **AD**.

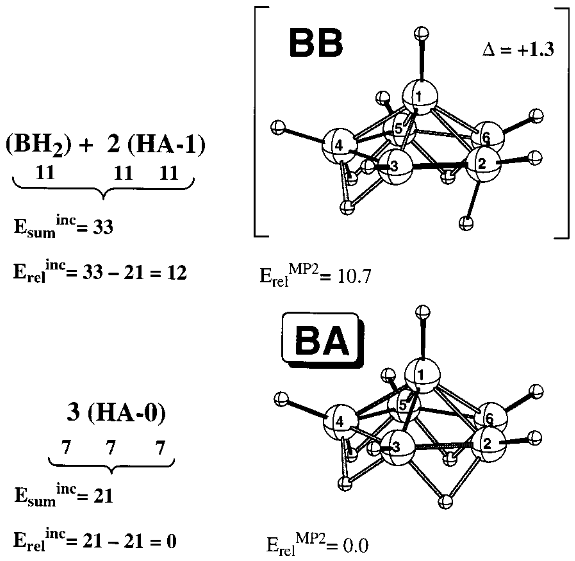


Figure 4. Isomers of *nido*-B_6H_{10}, **BA** and **BB**.

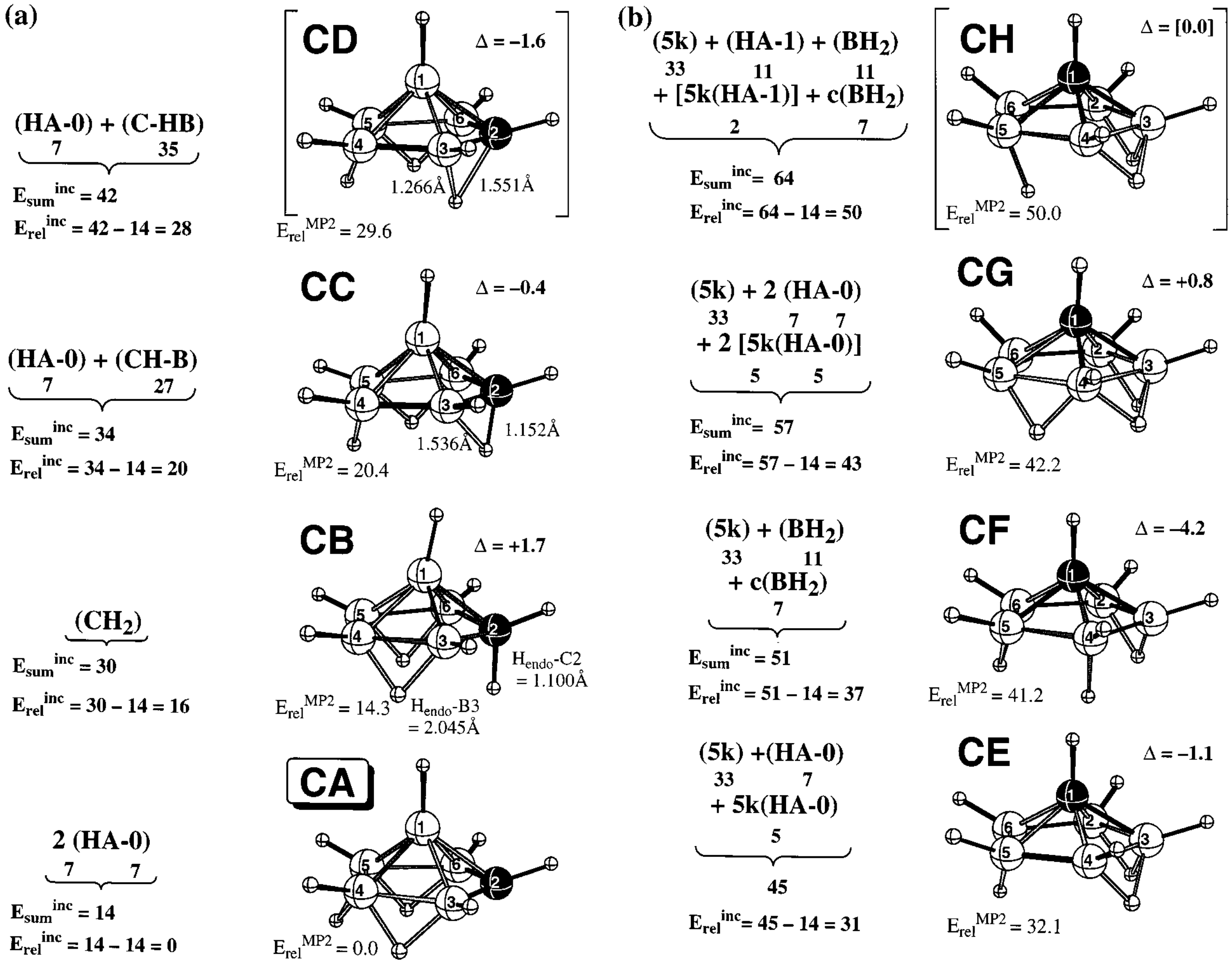


Figure 5. (a) Isomers of *nido*-$C_1B_5H_9$, **CA** to **CD**. (b) Isomers of *nido*-$C_1B_5H_9$, **CE** to **CH**.

is closer to the boron than to the carbon; an energy penalty of 35 kcal mol^{-1} is assigned. When a carbon atom is adjacent to either kind of CHB bridge hydrogen, c(CHB), an additional energy penalty of 5 kcal mol^{-1} is exacted. Last, all situations where one carbon is adjacent to another carbon (CA) incur a penalty of 15 kcal mol^{-1}.

The bridge hydrogen distances from neighboring carbon and boron atoms in the two kinds of bridge hydrogens, CH−B, and C−HB, are in Table 3, which is available as Supporting Information.

3.2. Penalties Associated with Unfavorable Skeletal Hydrogen Placements. The lower seven entries in Table 1 involve unfavorable skeletal hydrogen placements of two types. The first three involve BH_2 groups; the lower four involve BHB bridge hydrogens. The *endo*-BH in a BH_2 group (BH_2) incurs an energy penalty of 11 kcal mol^{-1}, but if it is adjacent to one carbon, c(BH_2), or two carbons, c(BH_2)c, additional penalties of 7 or 25 kcal mol^{-1} apply. The last four entries involve adjacent bridge hydrogens (HA). We identify two different skeletal electron bonding distributions. Both bonding situations result in the association of a cluster of six heavy boron−carbon skeletal atoms into pentagonal pyramidal configurations.

The labels 0−62 and 1−43 (which are discussed in the following section) identify these two skeletal electron bonding situations. Adjacent bridge hydrogen features (HA) should incur different penalty values when present in these two different electronic environments (0−62 and 1−43). Accordingly, an adjacent bridge hydrogen feature in the more common 0−62 “electronic environment” is identified by the symbol HA−0 associated with an energy penalty of 7 kcal mol^{-1}. When an apex carbon is also present, 5k(HA−0), an additional energy penalty of 5 kcal mol^{-1} is imposed. In contrast, the same adjacent bridge hydrogen feature in the more electron deficient

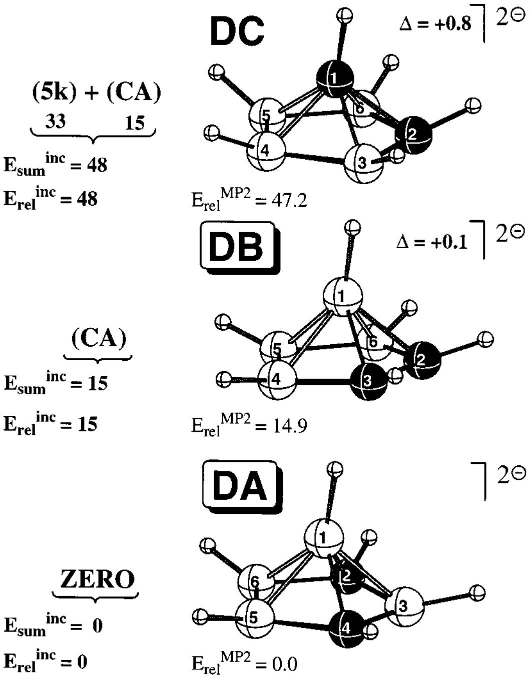


Figure 6. Isomers of *nido*-$C_2B_4H_6^{2-}$, **DA**, **DB**, and **DC**.

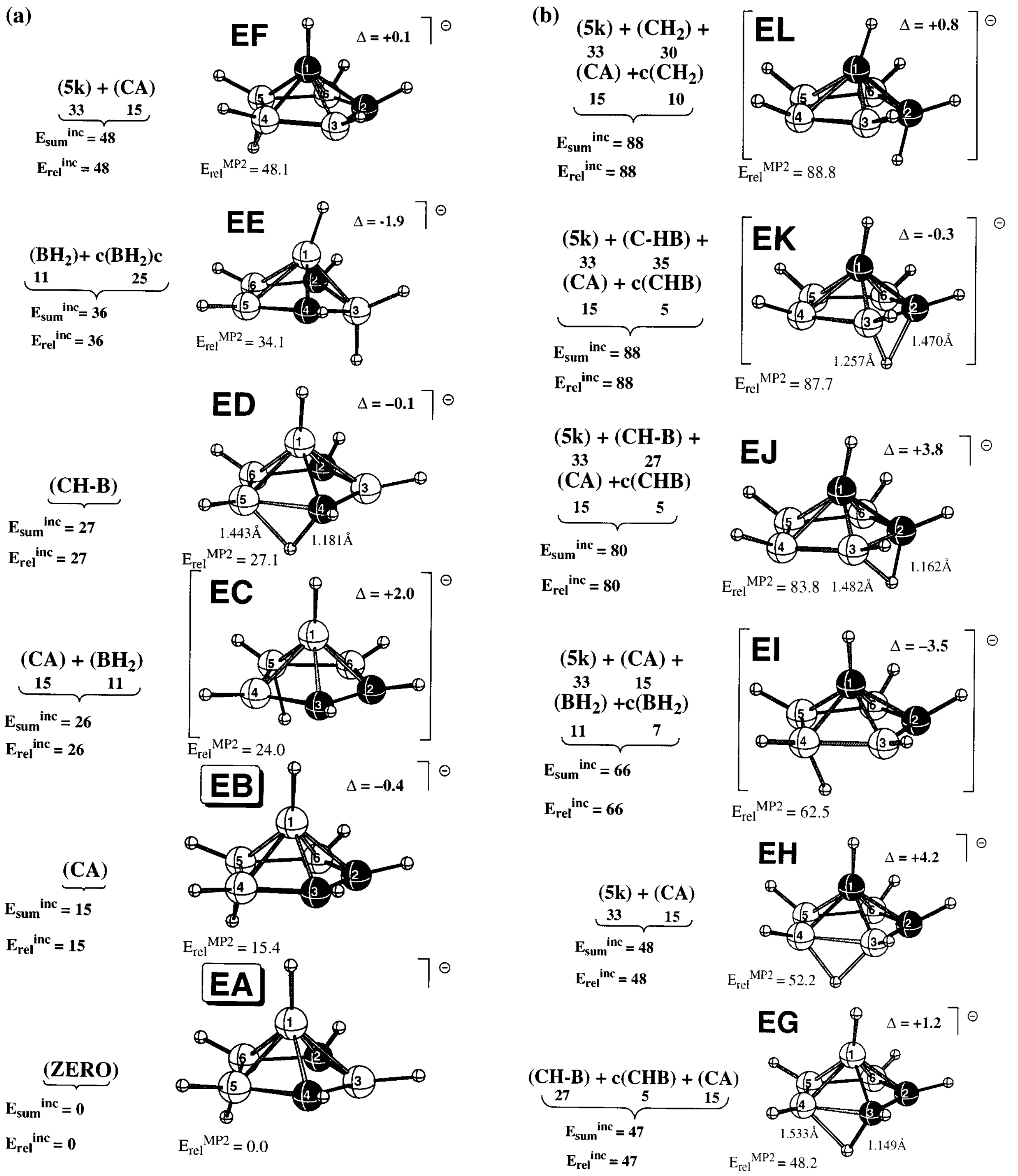


Figure 7. (a) Isomers of *nido*-$C_2B_4H_7^{1-}$, **EA** to **EF**. (b) Isomers of *nido*-$C_2B_4H_7^{1-}$, **EG** to **EL**.

1−43 environment is identified by the symbol HA−1 associated with an energy penalty of 11 kcal mol^{-1}. When an apex carbon is also present, 5k(HA−1), an additional energy penalty of 2 kcal mol^{-1} is imposed.

3.2.1. Two Different Skeletal Electron Pair Bonding Distributions, 0−62 and 1−43 (i.e., the P−ST Numbers) Characterize the *nido*-6⟨V⟩ Configurations.[8] All *closo*-carboranes may be considered to have their atoms located at sites (vertexes) on the surfaces of two concentric "spheres" or deltahedra.

(A) *The all-important skeletal borons and carbons* occupy sites located at the vertexes of the inner sphere (or of the inner deltahedron) and are held together by the *skeletal electron pair bonds.*[7,8] These are the electron pairs (illustrated as broken line bonds in Scheme 1) that are identified in both Lipscomb's and Wade's electron counting procedures.

(B) In contrast, *the less important but "omnipresent" exo-terminal hydrogens or other groups* occupy sites located at the vertexes of the outer sphere (or of the outer deltahedron) and are connected to the inner-sphere borons and carbons

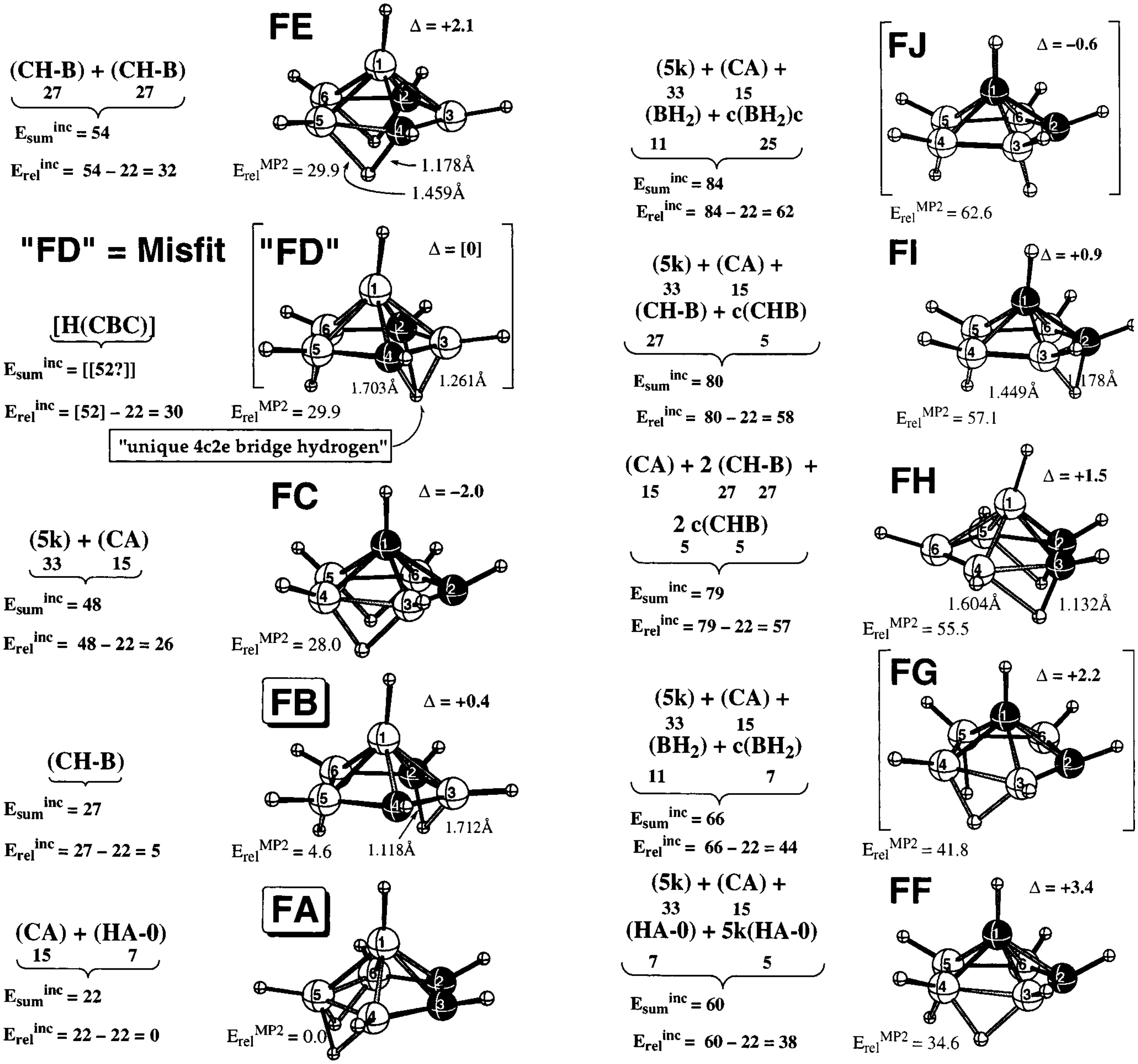


Figure 8. (a) Isomers of *nido*-$C_2B_4H_8$, **FA** to **FE**. (b) Isomers of *nido*-$C_2B_4H_8$, **FF** to **FJ**.

by the *exo-terminal electron pairs.* All *exo-terminal hydrogens or other exo-terminal groups and the exo-terminal electron pairs* are ignored, i.e., are not counted (see ○ = BH groups in Scheme 1).

(C) *The skeletal hydrogens* (both endo-bridge and endo-terminal), as well as the skeletal borons and carbons, occupy sites located on the surface of the inner deltahedron and are held together by the *skeletal electron pair bonds.* For simplification, the presence or absence of any skeletal endo-bridge hydrogens associated with two peripheral borons is ignored (see the $\pm H_b$ moieties in Scheme 1) and such bonds are artificially counted as a 2c2e B−B bonds *(when in actuality many may be in 3c2e BHB situations).* The presence or absence of a skeletal endo-terminal hydrogen on one boron is also disregarded (see the $\pm H_e$ moiety in the 1−43 isomer in Scheme 1) and artificially counted as a 1c2e bond (i.e., a skeletal lone pair) when it actually may be in a 2c2e situation. The presence of an endo-pair of electrons on a skeletal boron (a lone pair) is similarly treated as a 1c2e bond.

All *closo* compounds involve $n + 1$ skeletal electron pairs, which, in all *closo* six-atom species, equal *seven* electron pairs (see boxed area of Scheme 1). All *nido* compounds involve $n + 2$ skeletal electron pairs, which, in all *nido* six-atom species, must equal *eight* electron pairs (see the 0−62 and 1−43 configurations of *nido*-B_6H_{10} in Scheme 1).

Usually zero 1c2e bonds (“lone pairs”) are present, and thus, the 1c2e, −2c2e, 3c2e bond distributions are generally labeled 0−62, and all eight (6+2) of the 2c2e and 3c2e bonds hold the boron−carbon cluster together (see top left illustration in Scheme 1). In contrast, when one endo hydrogen or one endo lone pair is present, it is described as a 1−43 distribution. In the 1−43 distribution, only seven bonds (*four* 2c2e and *three* 3c2e bonds) hold the six-atom boron−carbon skeletal cluster together. In other words, the arrogation of *one* electron pair from the skeletal electron pair pool of *eight* into an endo lone-pair or an endo hydrogen (1c2e bond) on only one skeletal boron or carbon leaves only *seven* electron pairs to associate the six skeletal borons and carbons, 1−43. The six-atom boron−carbon

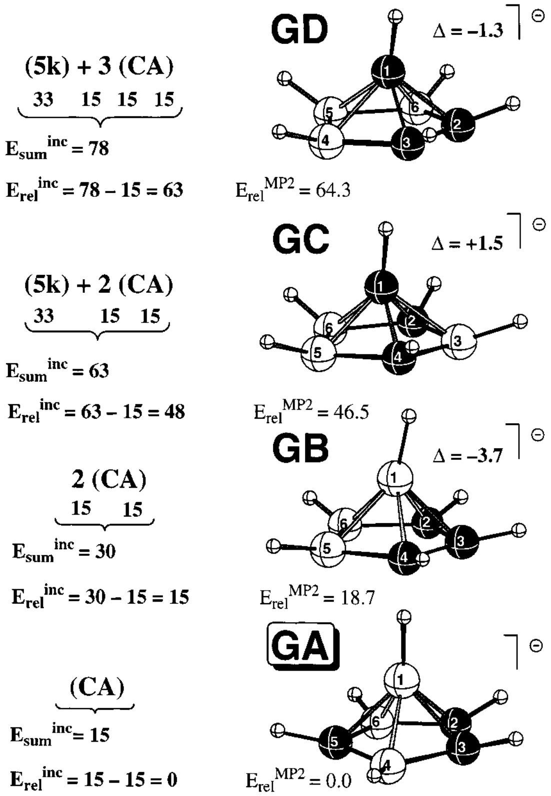


Figure 9. Isomers of *nido*-$C_3B_3H_6^{1-}$, **GA** to **GD**.

skeleton thus becomes "effectively" more electron-deficient as reflected by the increased number of 3c2e bonds, i.e., 0−6*2* → 1−43. The *four* 2c2e and *three* 3c2e bonds furnish only 17 "connections", but only 17 are needed in this case because the one endo 1c2e bond ensures that all six skeletal atoms gain access to an octet of electrons when the exo-terminal bonds are included.

Consider the increasing number and fraction of 3c2e bonds relative to all *"skeletal connecting bonds"*, e.g., two out of eight ($^2/_8 = 0.25$) in the 0−62 distribution and three out of seven ($^3/_7 = 0.43$) in the 1−43 distribution, which in part reflect a measure of the electron deficiency. Thus, a *nido*-6⟨V⟩ (1−43) compound with a 3c2e/(2c2e + 3c2e) ratio of 0.43 is about "half way" between the less electron-deficient *nido*-6⟨V⟩ 0−62 compound with a ratio of 0.25 and the more electron-deficient *closo*-6⟨III⟩ 0−34 compound with a ratio of 0.57 (see boxed portion in Scheme 1).

The penalties for certain architectural features are more pronounced the greater the electron deficiency, which increases in the order *hypho* < *arachno* < *nido* < *closo*.[23] Thus, it was anticipated that architectural features in the relatively more electron-deficient *nido*-6⟨V⟩ 1−43 species (which, arguably, are more like *closo* species than are the *nido*-6⟨V⟩ 0−62 species) would incur a somewhat greater energy penalty. It follows that an adjacent bridge hydrogen feature, $(BHB)_2$, in a 1−43 structure (HA−1) would incur a greater assigned penalty of 11 kcal mol^{-1} than an adjacent bridge hydrogen feature, $(BHB)_2$, associated with a 0−62 structure (HA−0) where the assigned penalty is only 7 kcal mol^{-1}. The symbol HA−1 is used to reflect the architectural feature of adjacent bridge hydrogens, $(BHB)_2$, in a 1−43 structure, while HA−0 is used to reflect the architectural feature $(BHB)_2$ in a 0−62 configuration. When the 5k(HA−1) and 5k(HA−0) symbols appear, it means that a carbon also occupies the 5k apex site and that additional penalties of 2 and 5, respectively, should be added.

3.3. Comparisons of Relative Stabilities from Empirical Energy Penalty Handicapping ($E_{\mathrm{rel}}^{\mathrm{inc}}$) and from ab Initio Calculated Values ($E_{\mathrm{rel}}^{\mathrm{MP2}}$). The various known and candidate structures are ordered with the lowest energy isomer at the bottom in Figures 3−13. Transition structures are in brackets. The ab initio calculated relative energies, $E_{\mathrm{rel}}^{\mathrm{MP2}}$ in kcal mol^{-1}, are to the lower left of the structures. The sums of the detrimental architectural energy increment penalty values, $E_{\mathrm{sum}}^{\mathrm{inc}}$, in kcal mol^{-1}, are summed along the left side of the figures. The differences, Δ values, between the the ab initio calculated values of $E_{\mathrm{rel}}^{\mathrm{MP2}}$ and penalty increment $E_{\mathrm{rel}}^{\mathrm{inc}}$ values are noted at the upper right of each of the molecular structures; e.g., the difference, Δ, of $E_{\mathrm{rel}}^{\mathrm{MP2}}$ and $E_{\mathrm{rel}}^{\mathrm{inc}}$ in the isomer **AC** is −3.5 in Figure 3.

3.3.1. *nido*-$B_6H_9^{1-}$ Isomers AA to AD. The compound *nido*-$B_6H_9^{1-}$ (see Figure 3) is fluxional; the three bridge hydrogens migrate about the base, rendering the five basal borons equivalent in the ^{11}B NMR spectrum even at very low temperatures.[26] The most stable structure, **AA** (known compounds are boxed), can easily rearrange into an identical **AA′**, etc. via the transition state **AB**.

3.3.2. *nido*-B_6H_{10} Isomers BA and BB. In *nido*-B_6H_{10} (see Figure 4) the four bridge hydrogens of *nido*-B_6H_{10} rapidly migrate about the base, making the five basal borons equivalent in a room temperature ^{11}B NMR spectrum. Apparently **BA** rearranges into **BA′**, etc. easily via transition state **BB**. Shore has "quenched" this fluxional behavior at low temperatures.[26]

3.3.3. *nido*-$C_1B_5H_9$ Isomers CA to CH. The only known *nido*-$C_1B_5H_9$ isomer, **CA** (see Figure 5) is static at room temperature;[27] no evidence for the other five isomers has been reported. Given the fluxional propensities of the carboranes, it may be that most of the other isomers, **CB** to **CH**, will never be detected.

3.3.4. *nido*-$C_2B_4H_6^{2-}$ Isomers DA to DC. The known isomers of *nido*-$C_2B_4H_6^{2-}$, **DA** and **DB** (see Figure 6) are static at room temperature, and there is no evidence for isomer **DC**. Because no skeletal hydrogens are present, the stability order **DA**, **DB**, **DC** is easily predictable on the basis of carbon placement rules A and B (see Introduction) and the $E_{\mathrm{rel}}^{\mathrm{inc}}$ values agree well with the $E_{\mathrm{rel}}^{\mathrm{MP2}}$ values.

3.3.5. *nido*-$C_2B_4H_7^{1-}$ Isomers EA to EL. The 12 configurations for *nido*-$C_2B_4H_7^{1-}$ illustrated in parts a and b of Figure 7 are produced when a proton is added to the *nido*-$C_2B_4H_6^{2-}$ structures (**DA, DB**, and **DC**). Of the two known isomers, **EA** is static at room temperature while the bridge hydrogen in **EB** oscillates from side to side like a "wind shield wiper" at room temperature via the transition state **EC**. Isomers with $E_{\mathrm{rel}}^{\mathrm{inc}}$ or $E_{\mathrm{rel}}^{\mathrm{MP2}}$ values above 30 or 40 kcal mol^{-1} are unlikely to be isolated. The isomers **EF** and **EH** interconvert via transition structure **EI**.

3.3.6. *nido*-$C_2B_4H_8$ Isomers FA to FH. The formal addition of two protons to the *nido*-$C_2B_4H_6^{2-}$ structures (Figure 6) produces the 10 configurations for *nido*-$C_2B_4H_8$ in parts a and b of Figure 8. The compound *nido*-$C_2B_4H_8$, **FA**, the first *nido*-carborane discovered and structurally characterized, was reported in 1962.[28] As expected, it is static at room temperature. It was bewildering when a novel structure (deduced from an ^{11}B NMR spectrum) appeared in poster session IMEBORON-

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(26) Shore, S. G.; et al. *J. Am Chem. Soc.* **1963**, *85*, 3167; *J. Am Chem. Soc.* **1965**, *87*, 3513.

(27) Onak, T. P.; Dunks, G. B.; Spielman, J. R.; Gerhart, F. J.; Williams, R. E. *J. Am. Chem. Soc*, **1966**, *88*, 2061.

(28) Onak, T. P.; Williams, R. E.; Weiss, H. G. *J. Am. Chem. Soc.* **1962**, *84*, 2830.

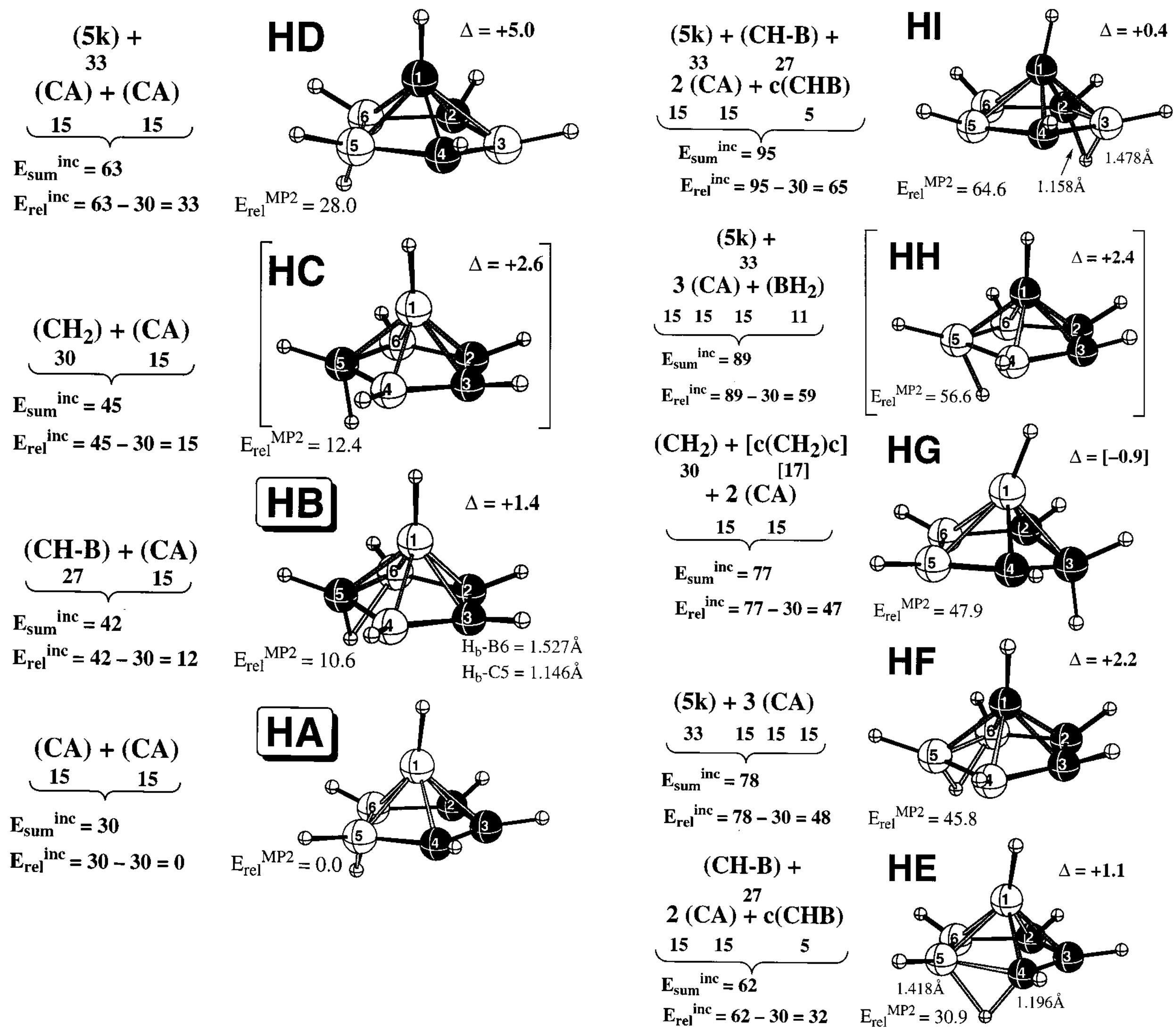

Figure 10. (a) Isomers of *nido*-$C_3B_3H_7$, **HA** to **HD**. (b) Isomers of *nido*-$C_3B_3H_7$, **HE** to **HI**.

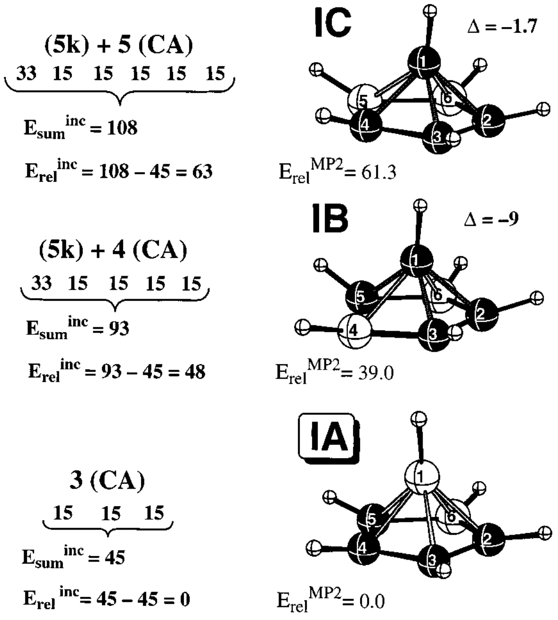

Figure 11. Isomers of *nido*-$C_4B_2H_6$, **IA** to **IC**.

IX in Heidelberg, July 1996,[3] which allegedly supported a structure related to a polyalkyl derivative of *nido*-CB_4H_8 (isoelectronic with *nido*-B_5H_9). This structure supposedly incorporated an electron-precise methylene group, making *two* skeletal endo-terminal attachments to the CB_4 skeletal cluster. No other *nido*-B_5H_9 analogue incorporating *one*, let alone *two*, endo-terminal attachments was known or had been hypothesized.

Several of us were skeptical of the structure when it was first made public in 1996.[29] We favored an alternative structural assignment in which the carbon of the presupposed methylene group was melded into the electron-deficient cluster structure, converting the pendant four-coordinated methylene group into a five-coordinated cluster carbon with endo and exo groups. The resulting structure would be a polyalkyl derivative of a new isomer of *nido*-$C_2B_4H_8$, i.e., **FB** in Figure 8, and would conform to the expected 0−62 configuration.[1,8]

Ab initio/IGLO/NMR calculations subsequently proved **FB** to be the correct structure. The CHB bridge-hydrogen is closer to one carbon but can be considered as a bridge-hydrogen between one carbon and a neighboring boron.[4] The two carbons in **FB** are not equivalent on an NMR time scale; thus, the CHB bridge-hydrogen is not fluxional; i.e., it does not exchange between the two otherwise equivalent carbon−boron peripheral edge locations. The "carbons-apart" isomers are most stable when one or no bridge hydrogens are present (see **DA** in Figure

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(29) Wrackmeyer, B.; Schanz, H.-J.; Milius, W. Presented at IMEBORON IX, Poster Session, Heidelberg, Germany, July 14−18.

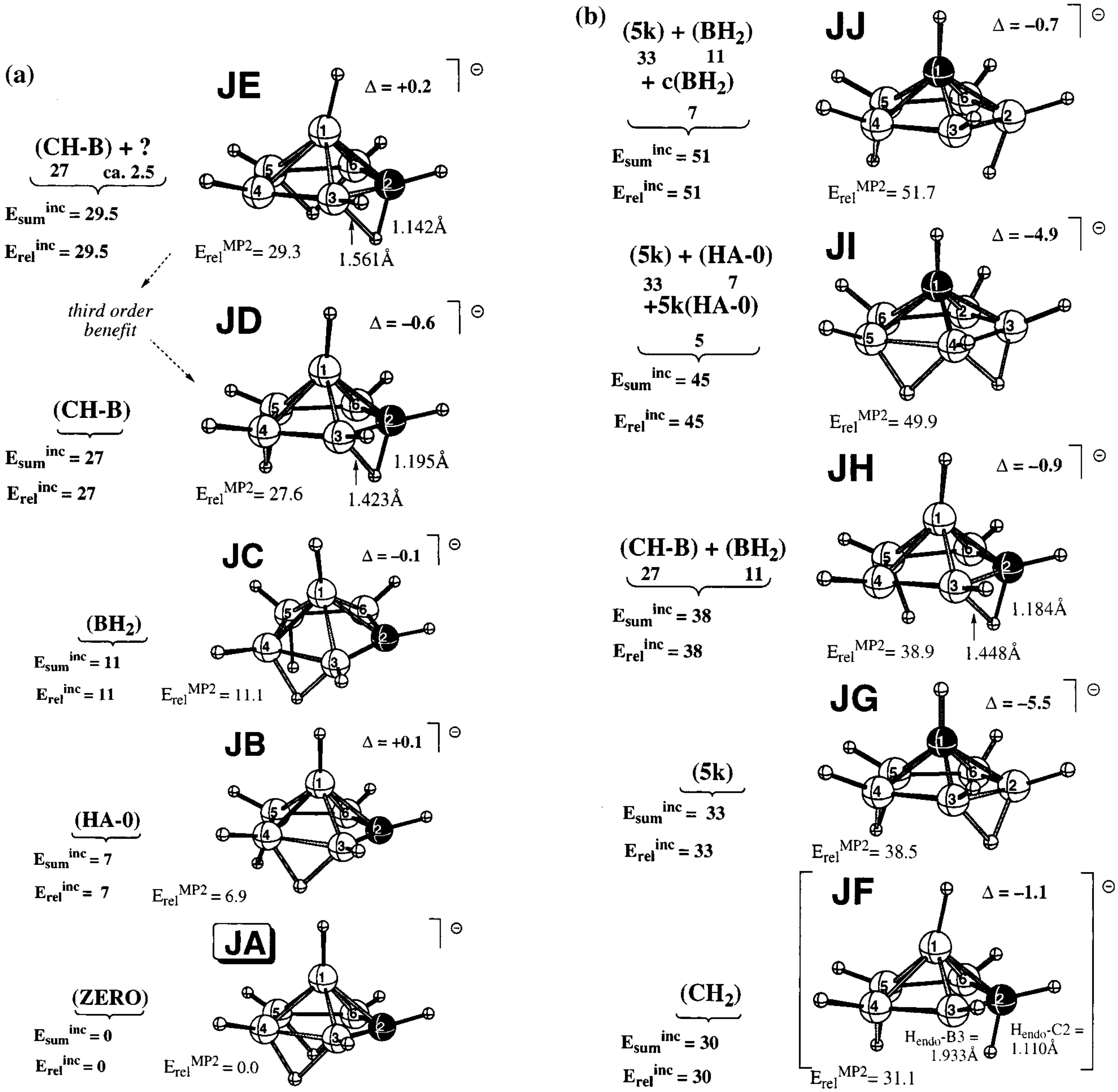

Figure 12. (a) Isomers of *nido*-$C_1B_5H_8^{1-}$, **JA** to **JE**. (b) Isomers of *nido*-$C_1B_5H_8^{1-}$, **JF** to **JJ**.

6 and **EA** in Figure 7). But when two skeletal hydrogens are present, the most stable isomer is the carbons' adjacent isomer **FA**, which provides optimal locations for the skeletal bridge-hydrogens between the borons.

Apparently there is a much smaller penalty in moving a carbon from a 3k site to a 4k site in **5** (Figure 1) as opposed to the much greater penalty of moving a 3k carbon to a 5k site in **FD**. Wrackmeyer's compound, **FB**, was only 4.6 kcal mol^{-1} less stable than **FA**. For isomer **FE** with two CHB bridge hydrogens the difference between the $E_{\mathrm{rel}}^{\mathrm{inc}}$ and $E_{\mathrm{rel}}^{\mathrm{MP2}}$ values is −2.1 kcal mol^{-1}. The structure **FB** might be presumed to interconvert into its mirror image via the transition structure **FD**. Such interconversion, however, does not take place on an NMR time scale because of a high (25.3 kcal mol^{-1}) energy barrier between **FB** ($E_{\mathrm{rel}}^{\mathrm{MP2}} = 4.6$) and **FD** ($E_{\mathrm{rel}}^{\mathrm{MP2}} = 29.9$).[4]

FD turns out to be a "structural misfit" among the 73 structures in Figures 3−13. A retroactive explanation is required. In 1976[1] it was emphasized that there was a continuum of skeletal hydrogens with unalloyed bridge-hydrogens and endo hydrogens defining the extreme cases (see ref 1, p 120). In a previous paper[4] the "mixed" skeletal hydrogens were identified as *endo hydrogens* that had "partial bridge-hydrogen" character. We now favor an alternative description that identifies all such "mixed" skeletal hydrogens, which are biased toward either a neighboring boron or carbon, as *bridge-hydrogens*.

A review of the structures of **FB** (**10** in ref 4) and **FD** (**11** in ref 4) reveals the answer to this dilemma. Note the exaggerated "underslung" position of the presupposed endo hydrogen of the BH_2 group in **FD** (**11** in ref 4). Such an endo hydrogen in **FD** could be bonding to the two neighboring carbons as well as to the boron. Compare also **EE** in Figure 7b where a BH_2 group is located between two neighboring CH groups and where there is no bonding of the endo hydrogen to the adjacent carbons. **FD** thus incorporates one skeletal hydrogen bridging a triangular CBC facet, i.e., a four-center, two-electron bond (4c2e). There are no similar features among the other 72 structures; thus, the **FD** structure must be separated from our other comparisons. The $E_{\mathrm{rel}}^{\mathrm{inc}}$ value of such a H(CBC) feature (H(CBC) ≈ 52± kcal mol^{-1}) would be impossible to rationalize with the $E_{\mathrm{rel}}^{\mathrm{MP2}}$ value.

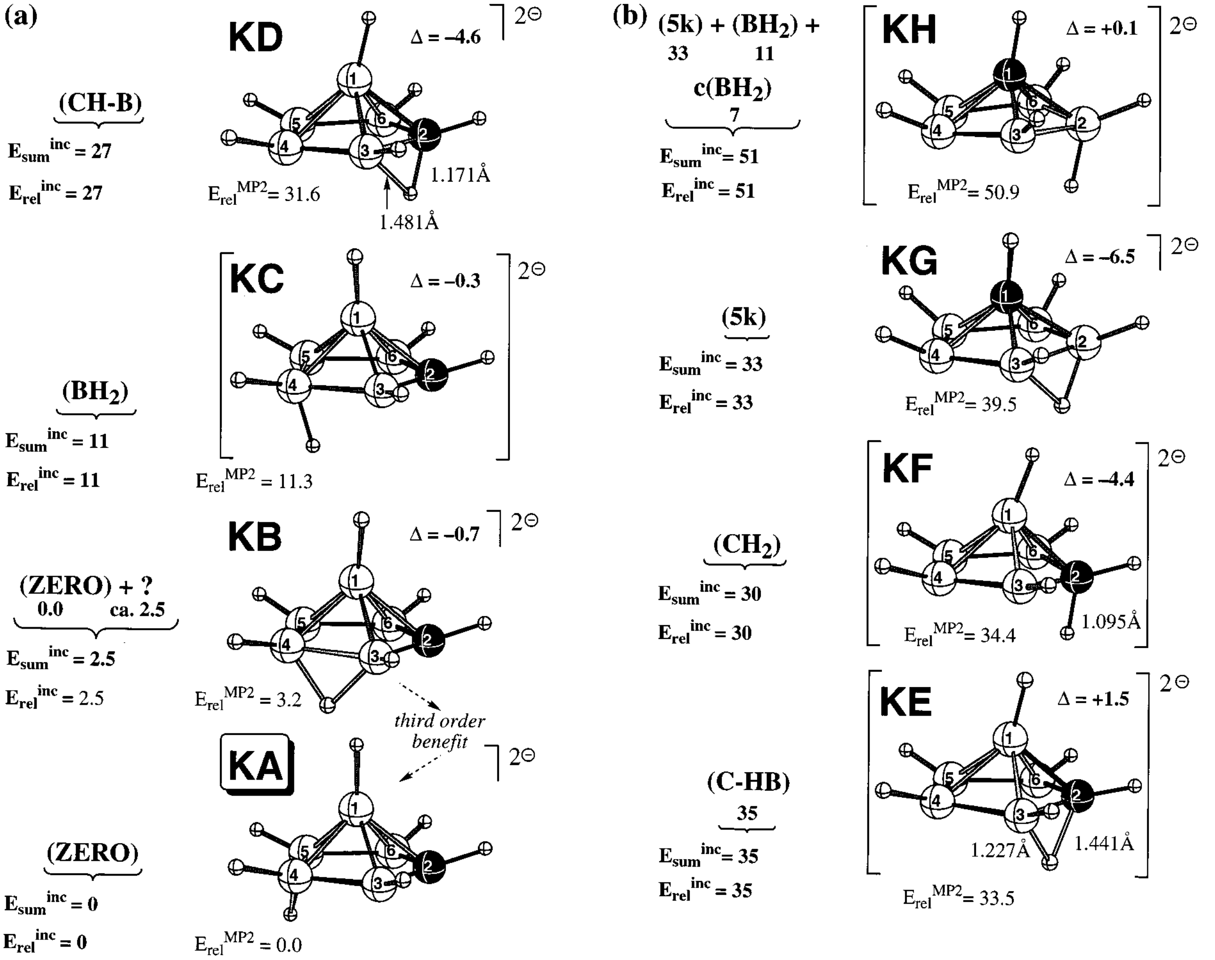

Figure 13. (a) Isomers of *nido*-$C_1B_5H_7^{2-}$, **KA** to **KD**. (b) Isomers of *nido*-$C_1B_5H_7^{2-}$, **KE** to **KH**.

3.3.7. *nido*-$C_3B_3H_6^{1-}$ Isomers GA to GD. There are no skeletal hydrogens in *nido*-$C_3B_3H_6^{1-}$, and the stability order is determined by the carbon placement rules. Hence, the carbon-apart isomer **GA** is most stable (see Figure 9).

3.3.8. *nido*-$C_3B_3H_7$ Isomers HA to HI. There is one skeletal hydrogen to accommodate in *nido*-$C_3B_3H_7$ (see parts a and b of Figure 10), and the known carbons-adjacent isomer, **HA**, is the most stable, as expected. The competition between carbon and skeletal hydrogen patterns parallel the situations illustrated in Figures 6−8. Siebert's carbons-apart isomer, **HB**,[2] is the next most stable. Because there are no adjacent peripheral borons in structure **HB** for a bridge hydrogen to be located, the skeletal hydrogen resides between the solitary carbon atom and a neighboring boron atom.

The ordering is "more than reversed" when comparing Siebert's **HB** (and its transition state **HC**) in Figure 10a[2] and Wrackmeyer's **FB** (and its transition state **FD**) in Figure 8a.[3] **HC** incorporates a legitimate CH_2 group; the endo terminal hydrogen lies between two uninvolved neighboring BH groups. **FD** incorporates an endo hydrogen bridging a boron and two neighboring carbons (a unique 4c2e bridge hydrogen). The bridging hydrogen atom is closer to the boron and is equidistant from its two neighboring carbon atoms. The barrier for rearrangement of **FB** into its mirror image **FB′** (via **FD)** is 25.3 kcal mol^{-1} and fluxionality is not observed in the NMR spectrum. The barrier for **HB** and its mirror image **HB′** (via **HC**) is only 1.8 kcal mol^{-1} and fluxionality is observed in the NMR spectrum, as expected.[2]

3.3.9. *nido*-$C_4B_2H_6$ Isomers IA to IC. In the absence of skeletal hydrogens the known isomer **IA**[30,31] for *nido*-$C_4B_2H_6$ (see Figure 11) is the most stable because it does not have a carbon in the 5k apex position. Among the remaining two isomers, which necessarily have one carbon in the 5k apex position, the basal carbons-apart isomer **IB** is more stable than the basal carbons-adjacent isomer **IC**. The difference value, Δ = −9 kcal mol^{-1}, between the E_{rel}^{inc} and E_{rel}^{MP2} values in **IB** is by far the largest difference encountered.

3.3.10. *nido*-$C_1B_5H_8^{1-}$ Isomers JA to JJ. In *nido*-$C_1B_5H_8^{1-}$ (see parts a and b of Figure 12) there are two skeletal hydrogens to accommodate and isomers avoiding 5k carbons, CH_2 groups, and CHB groups are found to have greater stability. As expected, **JD** is only slightly (ca. 2−3 kcal mol^{-1}) more stable than **JE** because the BHB bridge hydrogen is more remote from the offensive carbon (a third-order effect) in **JD**.

3.3.11. *nido*-$C_1B_5H_7^{2-}$ Isomers KA to KH. In *nido*-$C_1B_5H_7^{2-}$ (see Figure 13) there is one skeletal hydrogen to accommodate; avoiding 5k carbons and CHB groups is important. Again, **KA** is 2−3 kcal mol^{-1} more stable than **KB** because the BHB bridge hydrogen in KA is more remote from the offensive carbon (a third-order effect).

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(30) Fox, M. A.; Greatrex, R.; Nickrahi, A. *Chem. Commun.* **1996**, 175.

(31) (a) Binger, P. *Tetrahedron Lett.* **1966**, 715. (b) Onak, T. P.; Wong, G. T. F. *J. Am. Chem. Soc.* **1970**, *92*, 5226. (c) Pasinski, J. P.; Beaudet, R. A. *Chem. Commun.* **1973**, 928.

4. Conclusions

Ab initio relative energies and computed chemical shifts for various isomers of many different families of carboranes have resolved many structural disputes. These procedures have become firmly accepted during the 1990s. Less well-known or understood are the various structural features and skeletal electron bond distributions that underlie the numerical order in which the calculated ab initio relative energy values, E_{rel}^{MP2}, of the various isomers are found. This paper presents an effort to introduce some organization into this process. An "*empirical handicapping" of architectural features* in this *nido*-6⟨V⟩ set of 73 isomers was introduced and found to show good additive behavior. Energy increment penalty values can be summed up to provide E_{rel}^{inc} values that are remarkably close to the relative energy values, E_{rel}^{MP2}, computed at MP2(fc)/6-31G*. The same stability rankings result from both the E_{rel}^{inc} and E_{rel}^{MP2} values in all of the sets of isomers. Hence, it is unlikely that any of the primary architectural features responsible for the relative energies of the various isomers was missed.

A better understanding of CHB bridge hydrogens has been achieved. A less comprehensive empirical handicapping pattern accounted for the stability rankings of the *nido*-$C_4B_7H_{11}$ isomers,[16] but no E_{rel}^{inc} values were estimated because two kinds of $5k_C$ vertexes complicated the estimated "energy penalty" values. Further applications may be possible.

The 73 carboranes of this study have a pentagonal pyramidal geometry, i.e., a *nido*-6⟨V⟩ configuration, ordinarily with the 0−62 but occasionally with a 1−43 electron distribution. It has recently been shown that when electronegative elements N, O, and S are incorporated in place of carbon, the preferred structure may be the *nido*-6⟨*I*V⟩ configuration and the 1−43 electron distribution is probably much more prevalent.[32] The energy stabilities for both the *nido*-6⟨IV⟩ and the *nido*-6⟨V⟩ configurations were calculated in all cases, and additivity patterns based on elemental composition determined which configuration was preferred.

Supporting Information Available: Cartesian coordinates and absolute energies from MP2(fc)/6-31G* optimizations of $B_6H_9^-$ to $C_4B_2H_6$ structures discussed in the text, section 3.4 (CHB Endo-Bridge Hydrogens and Table 3), section 3.5 (Endo-terminal Hydrogens in BH_2 and CH_2 Groups and Table 4), Table 2 (Prevalence of Energy Penalties), and Figure 14 (Examples of Isomers Incorporating CHC Bridge Hydrogens). This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) Williams, R. E.; Ji, G.; Bausch, J. W. In *Contemporary Boron Chemistry*; Davidson, M. G., Hughes, A. K., Marder, T. B., Wade, K., Eds.; Royal Society of Chemistry: Cambridge, U.K., 2000.