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Energy–architectural patterns among the five- to twelve-vertex *closo*-carboranes[†]

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In 1969 the order of stabilities of all possible neutral two-carbon *closo*-carboranes, i.e. from *closo*-$C_2B_3H_5$ to *closo*-$C_2B_{10}H_{12}$, was forecast. It was wistfully anticipated that all 52 skeletal structures would be based solely upon the most spherical deltahedra (polyhedra consisting exclusively of triangular faces, *closo-n*$\langle$III$\rangle$; $n = 5$ to 12) and that the order of stabilities would be based upon the presumed preference of the two carbon atoms to occupy (a) low-coordinated and (b) nonadjacent sites.

The 52 potential isomers reduce to 42 isomers upon optimization (using the DFT B3LYP/6-311G* level of theory and the Gaussian 94 program), as seven isomers rearrange spontaneously into more stable isomers and three isomers rearrange spontaneously into two structures incorporating four-membered open faces within which are accommodated both carbon atoms, in adjacent 4*k*-edge sites. The order of stability of the 'surviving' 42 *closo*-carborane configurations comports nicely with the 1969 projections with the exception of *three* intimately related *closo*-11 vertex isomers. An explanation for the marginally increased stability of these *three* intimately related *closo*-11 vertex isomers is offered. For the remaining 39 isomers, the differences, between the calculated and estimated stability values, seldom exceed 6 kcal mol^{-1}. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: *closo*-carborane; isomers; energy differences; vertex type

INTRODUCTION

Recently, exceptional success was achieved in assigning explicit energy penalties to specific architectural features and subsequently predicting the structural stabilities of 73 *nido*-6$\langle$V$\rangle$ structures, from $B_6H_9^-$ to $C_4B_2H_6$. These compounds incorporate bridge hydrogen atoms, as well as boron and carbon atoms. Significantly, only *two* kinds of vertex were involved, i.e. one 5*k*-cage and five 3*k*-edge vertices.[1] Fair success was achieved with a similar approach involving the nine possible *nido*-11$\langle$V$\rangle$ isomers of *nido*-$C_4B_7H_{11}$, which incorporate three types of vertex: two kinds of 5*k*-cage and one kind of 4*k*-edge vertex.[2] In contrast, only limited success was achieved in correlating the energy penalty–architectural features relationship for the much more complex *nido*-8$\langle$VI$\rangle$ and *nido*-8$\langle$V$\rangle$ families of compounds ($B_8H_{10}^{2-}$ to $C_4B_4H_8$) that incorporate *several* kinds of 3*k*, 4*k* and 5*k* vertices.[3] Looking for additional groups of carboranes that might be subject to analysis by the energy penalty–architectural features relationship, we decided to look at the entire series of *closo*-carboranes (52 potential isomers) that presumably would have closo-deltahedral structures (*closo-n*$\langle$III$\rangle$, where $n = 5$ to 12). The order of stabilities (not the relative stabilities) had been estimated prior to 1969[4] based upon the carbon atoms' predisposition to occupy low-connected nonadjacent sites on the various deltahedra.[5,6]

DISCUSSION

Figure 1 illustrates the various isomers of the smallest one- and two-carbon *closo*-carboranes, $CB_4H_5^-$ and $C_2B_3H_5$, and their calculated relative energies in kilocalories per mole. It is seen in the mono-carbon anions that the energy penalty for a carbon moving from a 3*k*-vertex to a 4*k*-vertex is 24.9 kcal mol^{-1}.

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†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

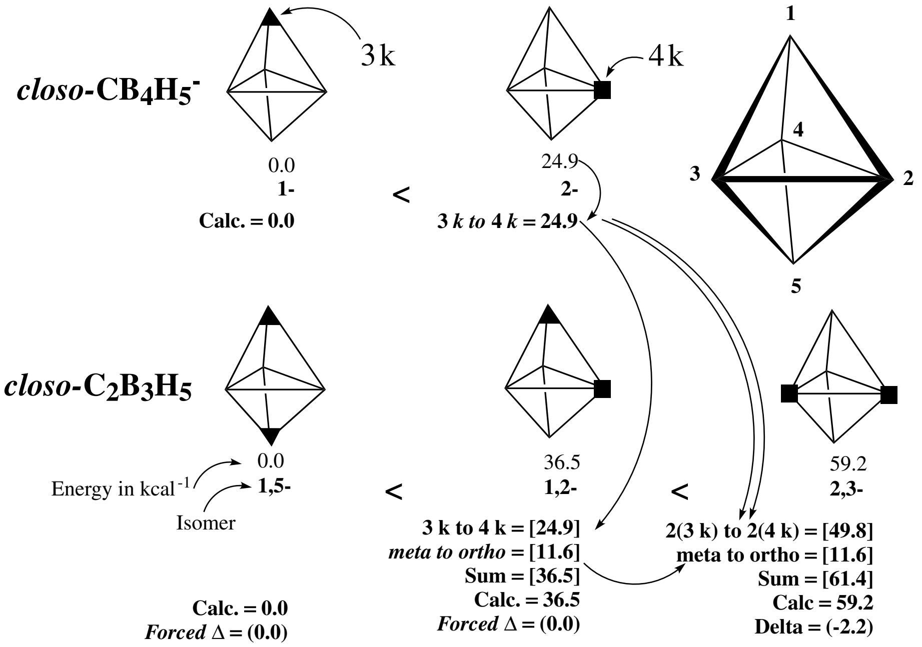

Figure 1. The *closo*-5<III> carboranes.

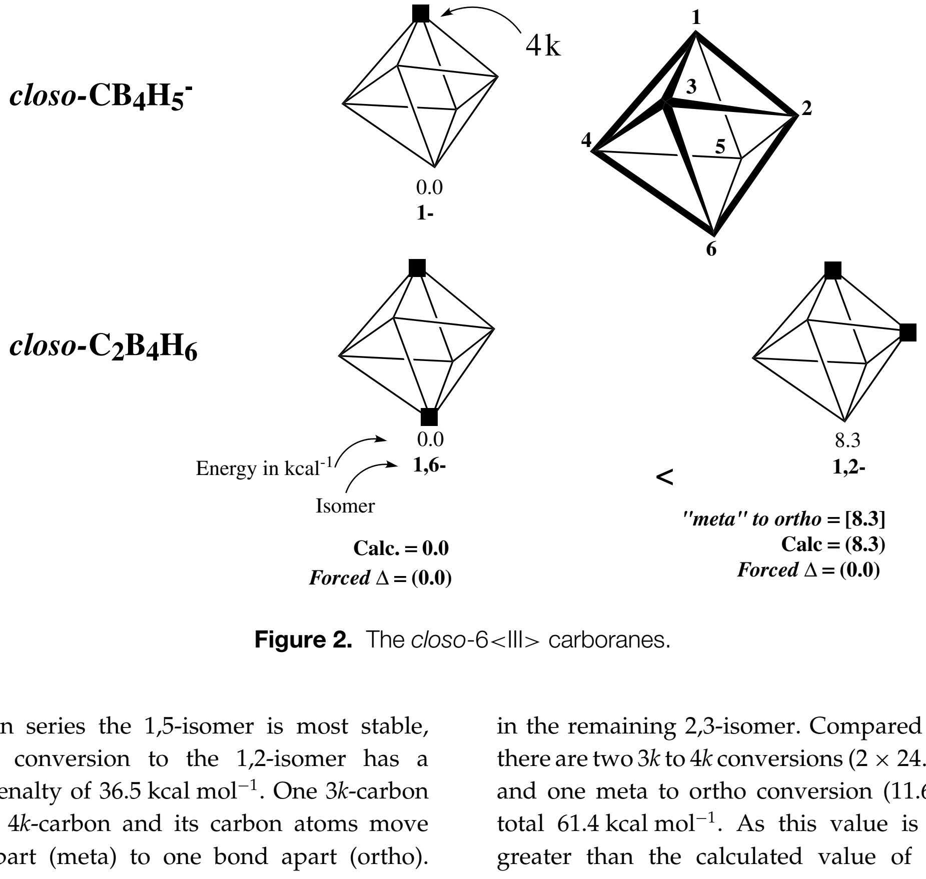

Figure 2. The *closo*-6<III> carboranes.

In the two-carbon series the 1,5-isomer is most stable, 0.0 kcal mol^{-1}, and conversion to the 1,2-isomer has a calculated energy penalty of 36.5 kcal mol^{-1}. One 3*k*-carbon is converted into a 4*k*-carbon and its carbon atoms move from two bonds apart (meta) to one bond apart (ortho). In order to match the calculated total value we must add 11.6 (a meta to ortho conversion penalty) to 24.9 (the 3*k* to 4*k* conversion penalty) to get the total value of 36.5 kcal mol^{-1}. These two 'forced' numbers can be tested in the remaining 2,3-isomer. Compared with the 1,5-isomer there are two 3*k* to 4*k* conversions ($2 \times 24.9 = 49.8$ kcal mol^{-1}) and one meta to ortho conversion (11.6 kcal mol^{-1}), which total 61.4 kcal mol^{-1}. As this value is only 2.2 kcal mol^{-1} greater than the calculated value of 59.2 kcal mol^{-1}, the correspondence is well within the anticipated range of 0–6 kcal mol^{-1}.

Figure 2 illustrates (for completeness only) the various isomers of the one- and two-carbon *closo*-carboranes $CB_5H_6^-$

and $C_2B_4H_6$ and their calculated relative energies in kilocalories per mole. No testing is possible, as only one kind of 4*k*-carbon is present and the only 'compulsory' or 'forced' energy penalty is the 8.3 kcal mol^{-1} for a meta to ortho conversion.

Figure 3 illustrates (for completeness only) the various isomers of the one- and two-carbon *closo*-carboranes $CB_{11}H_{12}^-$ and $C_2B_{10}H_{12}$ and their calculated relative energies in kilocalories per mole. Again, no testing is possible, as only one kind of 5*k*-carbon is present and the only 'forced' energy penalty values are the 2.8 kcal mol^{-1} for a para (three bonds apart) to meta conversion and an energy penalty of 18.8 kcal mol^{-1} for a para to ortho conversion.

Figure 4 illustrates the various isomers of the *closo*-carboranes $CB_6H_7^-$ and $C_2B_5H_7$ and their calculated relative energies in kilocalories per mole. Here, testing is possible, as both 4*k*- and 5*k*-carbon atoms are present. The 4*k*- to 5*k*-carbon energy penalty value is calculated from the 2- to 1-isomers to be 30.2 kcal mol^{-1}, whereas the meta to ortho energy penalty value from the 2,4- to 2,3-isomers is 16.6 kcal mol^{-1}. Testing these energy penalty values in the 1,2- and 1,7-isomers reveals mismatches of -5.9 kcal mol^{-1} and $+5.8$ kcal mol^{-1} respectively, which are at the borderline of acceptability.

Figure 5 illustrates the various isomers of the one- and two-carbon *closo*-carboranes $CB_7H_8^-$ and $C_2B_6H_8$ and their relative energies in kilocalories per mole. Testing is possible, as both 4*k*- and 5*k*-carbon atoms are present. However, the 4*k*- to 5*k*-carbon conversion penalty cannot be calculated by comparing the 1- and 3-mono-carbon isomers as the 3-isomer spontaneously optimizes into the 1-isomer.

At this juncture it should be stated that, among the *closo*-borane dianions, the *closo*-$B_8H_8^{2-}$ and *closo*-$B_{11}H_{11}^{2-}$ species indulge in wholesale fluxionality, yielding only one ^{11}B NMR chemical shift signal representing several kinds of boron atoms in each case. The $CB_7H_8^-$ and $C_2B_6H_8$ compounds are related to the *closo*-$B_8H_8^{2-}$ species, and fluxionality is to be expected. Later (see Fig. 8), species related to *closo*-$B_{11}H_{11}^{2-}$ are also shown to engage in fluxional behavior.

Comparing the 1,7-, 1,2- and 1,5-isomers of *closo*-$C_2B_6H_8$ with each other yields a meta to ortho energy penalty value of 21.9 kcal mol^{-1} and a 4*k* to 5*k* energy penalty value of 23.9 kcal mol^{-1} respectively. These values may be tested on the 1,6- and 3,4-isomers, which yield mismatches of -4.2 kcal mol^{-1} and $+4.9$ kcal mol^{-1} respectively. The projected order of stability is always correct, but the values are only fair. The 3,5-isomer, which is expected to be ~70 kcal mol^{-1} less stable than the 1,7-isomer, spontaneously optimizes into the 1,7-isomer. We will return to the probable mechanism in a later section.

The anticipated '1,3′-isomer (*closo*-8⟨III⟩) was extrapolated to have a calculated relative energy of ~41.6 kcal mol^{-1}, as it has architectural features equivalent to those of the comparable 1,6-isomer. However the '1,3′-isomer spontaneously optimizes into a structure with a square open face (*closo*-8⟨IV⟩), incorporating two adjacent 4*k* carbon atoms, that has a calculated relative energy of 31.2 kcal mol^{-1}. This deviant '1,3′-isomer (*closo*-8⟨IV⟩), with a relative stability value of 31.2 kcal mol^{-1}, may be compared to the 1,2-isomer (a *closo*-8⟨III⟩ structure incorporating two adjacent 4*k* carbon atoms); it has a relative stability value of 21.9 kcal mol^{-1}. The *closo*-8⟨III⟩ to *closo*-8⟨IV⟩ structural energy penalty appears to be ~9.3 kcal mol^{-1}.

Figure 6 illustrates the various isomers of the one- and two-carbon *closo*-carboranes $CB_8H_9^-$ and $C_2B_7H_9$ and their relative energies in kilocalories per mole. Both 4*k*- and 5*k*-carbon atoms are present. The 4*k*- to 5*k*-carbon conversion penalty (forced) is calculated from the 4- to 1-isomers to be 20.4 kcal mol^{-1}, and the meta to ortho value (forced) from comparing the 3,4- to 1,4-isomers is 13.6 kcal mol^{-1}. Testing these energy penalties in the 3,4-, 1,7- and 1,9-isomers reveals satisfactory mismatches of -3.2 kcal mol^{-1}, $+2.3$ kcal mol^{-1} and -0.1 kcal mol^{-1} respectively. One of the least stable isomers, the 1,2-isomer, spontaneously optimizes into the most stable 4,5-isomer.

Figure 7 illustrates the various isomers of the one- and two-carbon *closo*-carboranes $CB_9H_{10}^-$ and $C_2B_8H_{10}$ and their calculated relative energies in kilocalories per mole. Both 4*k*- and 5*k*-carbon atoms are present. The 4*k*- to 5*k*-carbon energy penalty value is calculated to be 20.9 kcal mol^{-1} by comparing the 1- and 2-anion isomers, and the neutral 1,10- and 1,6-isomers rationalize a 0.4 kcal mol^{-1} para to meta energy penalty. The 1,10- and 1,2-isomers suggest a 18.7 kcal mol^{-1} para to ortho energy penalty. These values are tested on the four sequentially less stable 2,7-, 2,4-, 2,6- and 2,3-isomers, where marginally acceptable mismatch values of -0.2 kcal mol^{-1}, $+4.2$ kcal mol^{-1}, -4.5 kcal mol^{-1} and -4.1 kcal mol^{-1} resulted respectively.

Figures 8 to 12 and Table 1 list the 'jungle' of the various isomers of the one- and two-carbon *closo*-carboranes $CB_{10}H_{11}^-$ and $C_2B_9H_{11}$. Figure 8 shows the calculated relative energies in kilocalories per mole of the five potential one-carbon isomers of $CB_{10}H_{11}^-$. One isomer incorporates a 4*k* carbon, 2-$CB_{10}H_{11}^-$, three isomers include 5*k* carbon atoms (10-, 8- and 4-) and one isomer features a 6*k* carbon (1-). To make the following discussions easier, the 11-vertex deltahedron may be viewed as a decaborane-shaped fragment, resembling a boat or canoe, 'capped' by a 6*k* vertex. The four 'gunwale' 5*k*-positions of the decaborane-like canoe fragment, i.e. the 4-, 5-, 6- and 7-positions, will be shown to be of extraordinary 'stability/instability' interest in the following figures and tables.

As expected, the most stable isomer of $CB_{10}H_{11}^-$ is the 2-isomer (0.0 kcal mol^{-1}). The 5*k*-carbon isomers (10- and 8-) are almost equivalent, averaging 19.7 kcal mol^{-1}, and the 6*k*-carbon isomer (1-) almost doubles the 'penalty' at 37.9 kcal mol^{-1}. The potential isomer 4-$CB_{10}H_{11}^-$ incorporates its carbon in a gunwale 5*k*-position but, upon optimization, it spontaneously rearranges into the most stable isomer, 2-$CB_{10}H_{11}^-$. From our 'carbon-centric' point of view we had anticipated that the 4-, 5-, 6-, 7- (gunwale-carbon) 5*k*-sites would be somewhat 'less desirable' locations for carbon than the 8-, 9-, 10- and 11- 5k-locations, as the former adjoin the

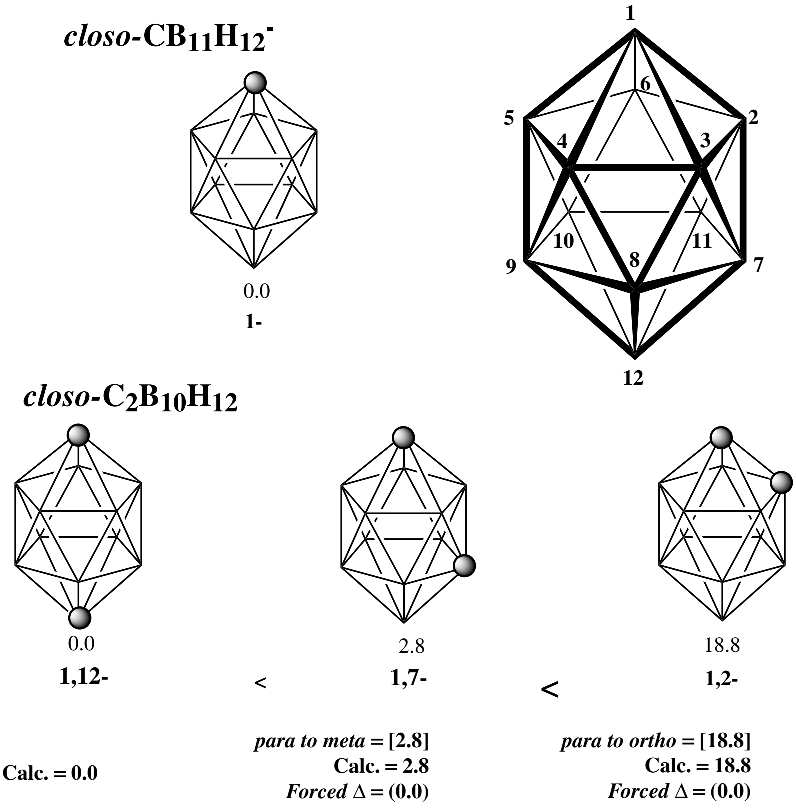

Figure 3. The *closo*-12<III> carboranes.

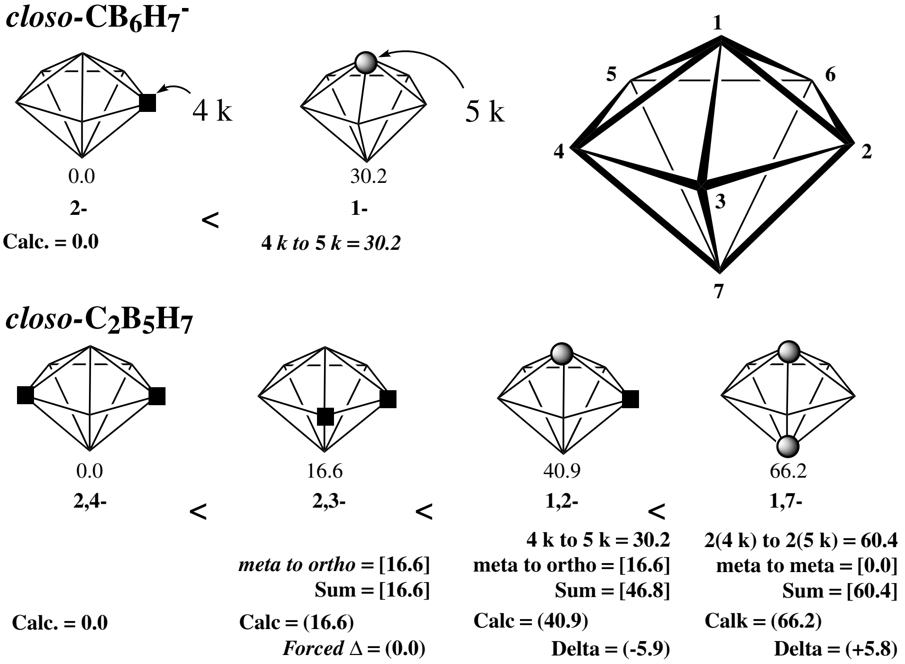

Figure 4. The *closo*-7<III> carboranes.

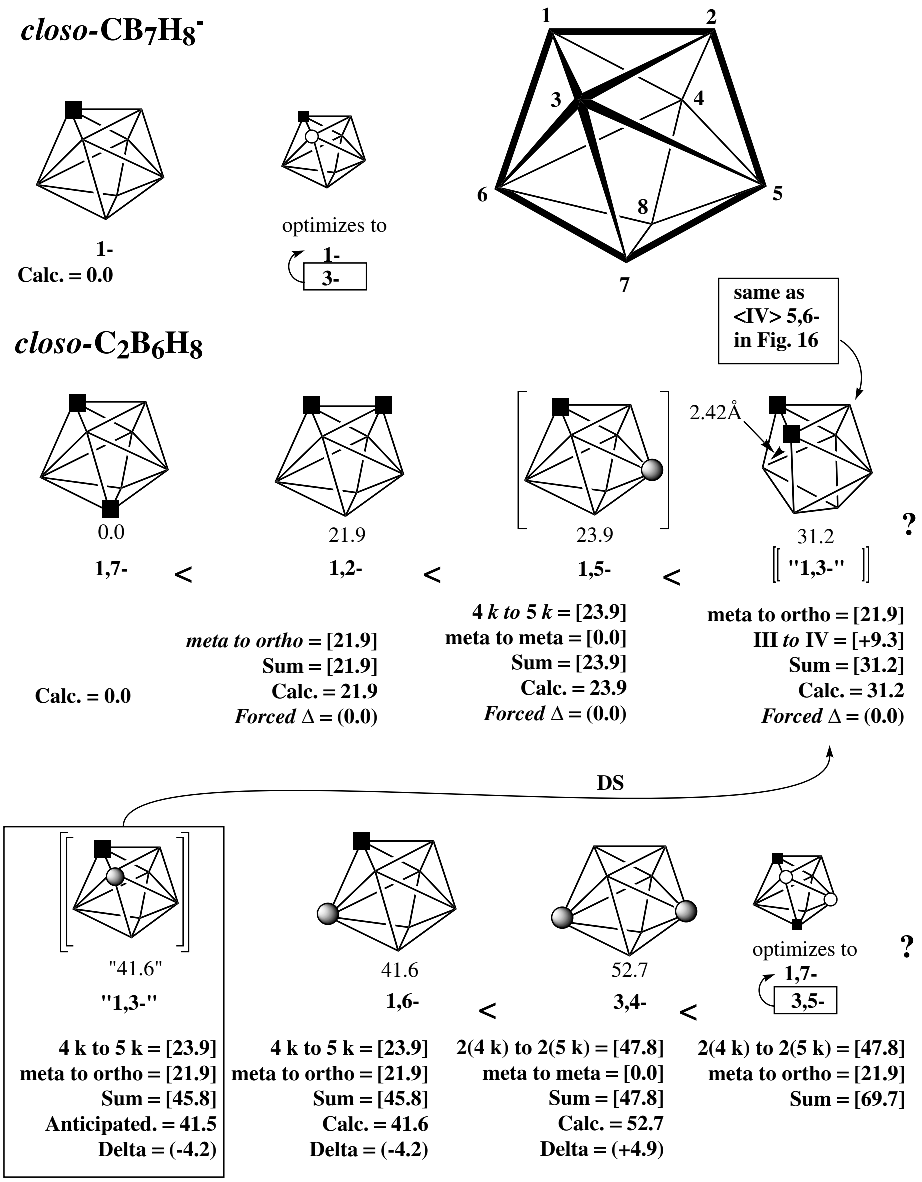

Figure 5. The *closo*-8<III> carboranes.

electron-'starved' 6*k* vertex. We would have expected an energy penalty of slightly more than 20.6 kcal mol^{-1} for the 4-$CB_{10}H_{11}^-$ isomer.

Figure 9 lists the 20 potential *closo*-11⟨III⟩ isomers of $C_2B_9H_{11}$. Upon optimization, seven isomers (all seven are in boxes) rearrange into more stable structures. Five isomers rearrange into three more stable *closo*-11⟨III⟩ isomers. Two isomers rearrange into a nonconforming *closo*-11⟨IV⟩ isomer with a square open face (those in solid-line boxes). Thirteen *closo*-11⟨III⟩ isomers remain.

Firstly, of the 20 potential isomers, seven incorporated one, and only one, carbon in a gunwale location and all seven of those isomers spontaneously rearranged to more stable isomers during optimization; see single heavy underlined isomer-notations in Figure 9. Secondly, and in complete contrast, the 13 isomers that did not rearrange incorporated either *zero* or *two* gunwale carbon atoms! Thirdly, and equally noteworthy, is the fact that *all three* possible isomers incorporating both carbon atoms in gunwale positions not only survived optimization (see double heavy underlined notation in Figure 9), but these three idiosyncratic 'two-gunwale-carbon' isomers (i.e. 4,6-, 4,5-, and 4,7-) tend to be several kilocalories per mole more stable than expected. It appears that one gunwale carbon is terminal in all cases but two gunwale carbon atoms are somehow beneficial (see also Table 1).

In Fig. 10, the 13 surviving *closo*-11⟨III⟩ isomers of $C_2B_9H_{11}$ are subjected to energy penalty evaluations. As expected,

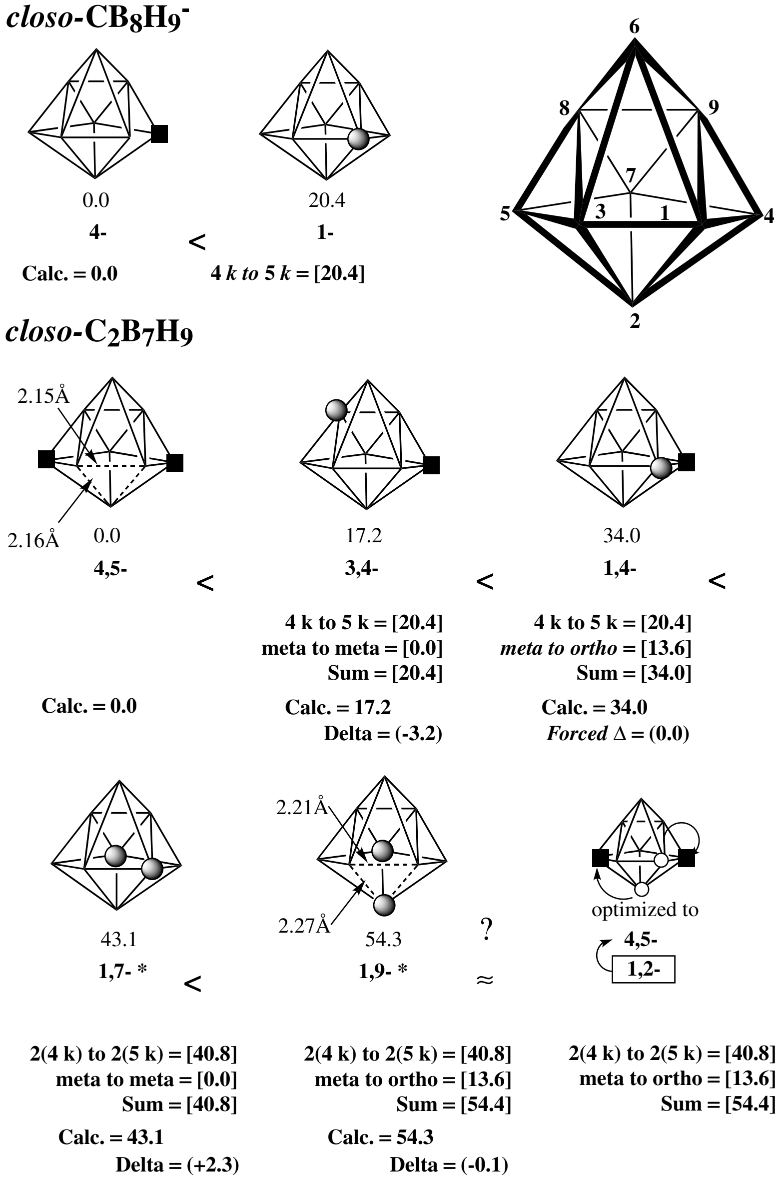

Figure 6. The *closo*-9<III> carboranes.

the known *closo*-2,3-$C_2B_9H_{11}$ isomer is calculated to be the most stable. The 2,9-isomer is assigned one 4*k* to 5*k* energy penalty of 19.7 kcal mol^{-1} (brought forward from Fig. 8). The addition of a 'forced' energy benefit of −2.3 kcal mol^{-1} for the meta to para transition yields the calculated 17.4 kcal mol^{-1} value for the 2,9-isomer. The 2,8-isomer is also assigned one 4*k* to 5*k* penalty of 19.7 kcal mol^{-1}, and a 'forced' penalty of 16.2 kcal mol^{-1} for a meta to ortho transition yields the calculated 35.9 kcal mol^{-1} value for the 2,8-isomer. The other ten isomers may now be evaluated using the aforementioned values plus the 4*k* to 6*k* penalty of 37.9 kcal mol^{-1} brought forward from Fig. 8.

Omitting, transiently, the eccentric three isomers (4,6-, 4,5- and 4,7-) that contain two gunwale carbon atoms, the mismatch values of −0.9, +0.3, −6.1, −5.2, −1.5, −1.8 and +2.0 kcal mol^{-1} are excellent except for the −6.1 and −5.2 kcal mol^{-1} values. The 1,2- and 10,11-isomers are calculated to be somewhat more stable than our estimates would have forecast. That the *closo*-1,2-$C_2B_9H_{11}$ isomer is more stable is probably related to the reasons that the 4,6-, 4,5- and 4,7-$C_2B_9H_{11}$ isomers are surprisingly stable (see Fig. 11), but we have no explanation for the 10,11-isomer's stability.

Figure 11 illustrates the 4,6-, 4,5- and 4,7-$C_2B_9H_{11}$ structures and perhaps why they are more stable than expected. At the top of Fig. 11 the *closo*-$B_{11}H_{11}^{2-}$ dianion reflects its vertex connectivities *k* on the left and crude negative charges on the variously connected vertices, which add up to the total charge of 2^-, on the right. Assuming the accompanying cations are

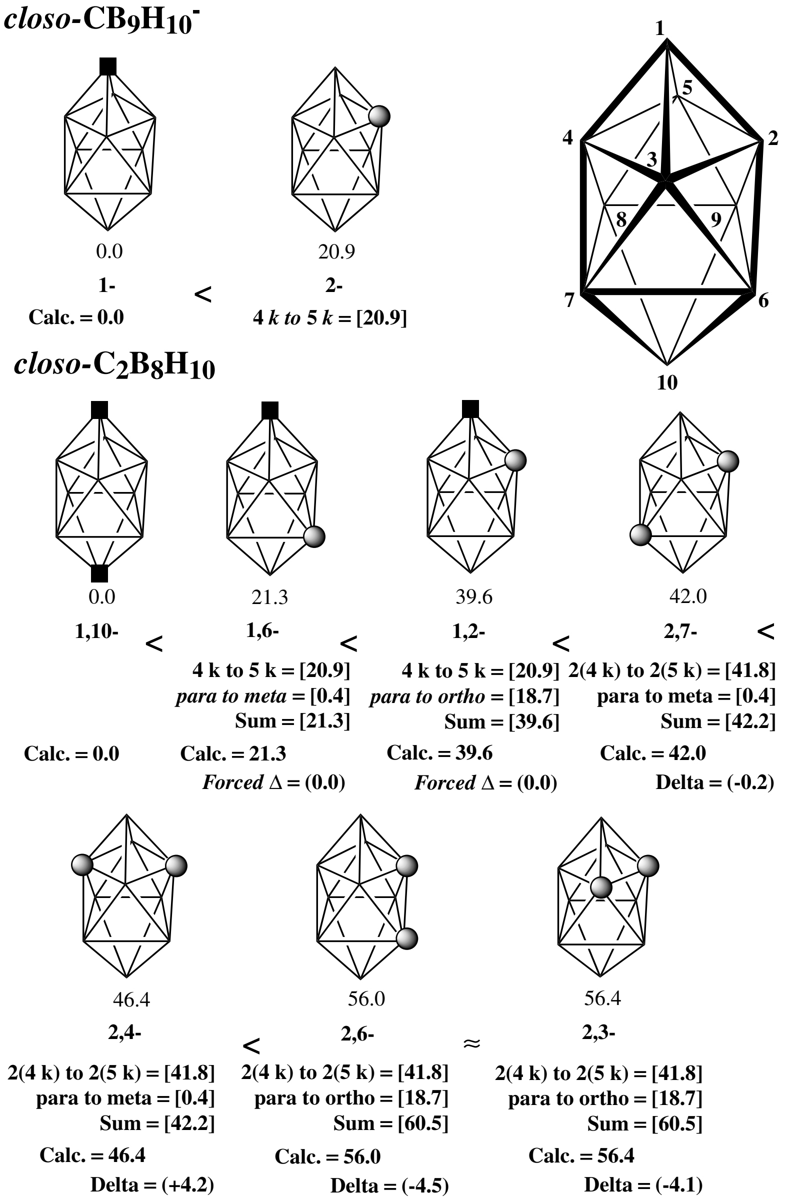

Figure 7. The *closo*-10<III> carboranes.

protons, $^1H^+$, one can notionally inject them into two ^{11}B atoms in the 2- and 3-positions of $B_{11}H_{11}^{2-}$, thus producing two ^{12}C atoms and a neutral *closo*-2,3-$C_2B_9H_{11}$ molecule; a simple transmutation of the elements.

According to our carbon-centric viewpoint, the carbon atoms are now in the best possible positions for carbon, i.e. in the lowest coordinated, nonadjacent, sites. This presumably accounts for the greatest stability of the 2,3-isomer. Perhaps we should consider a little boron-centric contribution to stability as well. One 6*k* boron is present and 6*k*-boron atoms are exceedingly rare in stable boranes and carboranes. If, hypothetically, the skeletal electron distribution in $B_{11}H_{11}^{2-}$ remained precisely the same after conversion to 2,3-$C_2B_9H_{11}$, the carbon atoms would become ∼4/6$^+$ charged. In actuality, we would expect substantial redistribution of the skeletal electrons in the direction of the two carbon atoms, driven by charge smoothing forces. This would benefit (skeletally electron enrich) the two 4*k* carbon atoms, but it might well benefit the 6*k*-boron atom also because of its proximity to the two 4*k* carbon atoms. In other words, the placement of two carbon atoms in the 2,3-positions is not only very good for the carbon atoms but also of some benefit to the 6*k* boron.

The first-order carbon-centric view is that desirability of location by carbon declines in the order 4*k* > 5*k* > 6*k*. A second-order effect might be inferred, i.e. that the 8-, 9-, 10- and 11-sites for 5*k* carbons (safely remote from the 6*k* vertex)

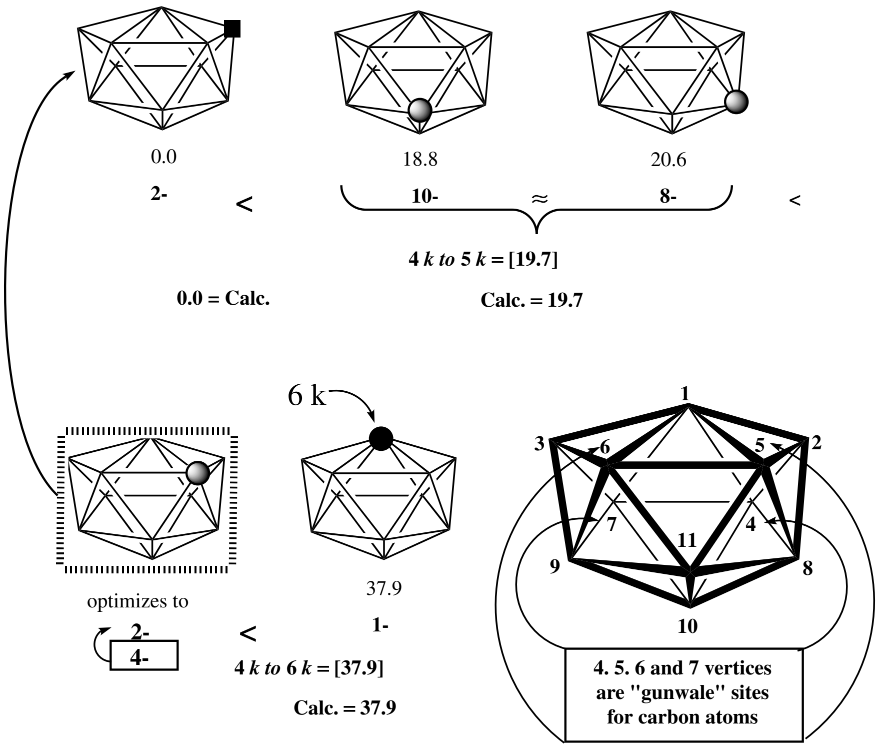

Figure 8. Five *closo*-$CB_{10}H_{11}^{-}$ structures reduce to four.

Table 1. *closo*-$C_2B_9H_{11}$ isomer characteristics

closo-$C_2B_9H_{11}$ Isomer		Relative energy (kcal mol^{-1})	Deserters' structural fate	One 'gunwale' carbon 'fatal'	Two 'gunwale' carbon atoms 'beneficial'	Unexpectedly stable
Survivors	Deserters					
2,3-		**0.0**				
2,9-		17.4				
	2,6-		2,3-	*2,6-*		
2,10-		18.8				
4,6-		**30.2**			**4,6-**	**4,6-** (by 9.4 kcal mol^{-1})
	2,4-		'2,4-' <IV>	*2,4-*		
	4,9-		2,3-	*4,9-*		
	4,11-		2,10-	*4,11-*		
4,5-		**34.3**			**4,5-**	**4,5-** (by 5.1 kcal mol^{-1})
2,8-		35.9				
8,9-		39.7				
4,7-		**40.4**			**4,7-**	**4,7-** (by 15.5 kcal mol^{-1})
1,2-		48.0				
10,11-		50.4				
	4,8-		2,10-	*4,8-*		
	4,10-		'2,4-' <IV>	*4,10-*		
8,10-		54.1				
1,10-		55.8				
1,8-		59.6				
	1,4-		2,3-	*1,4-*		

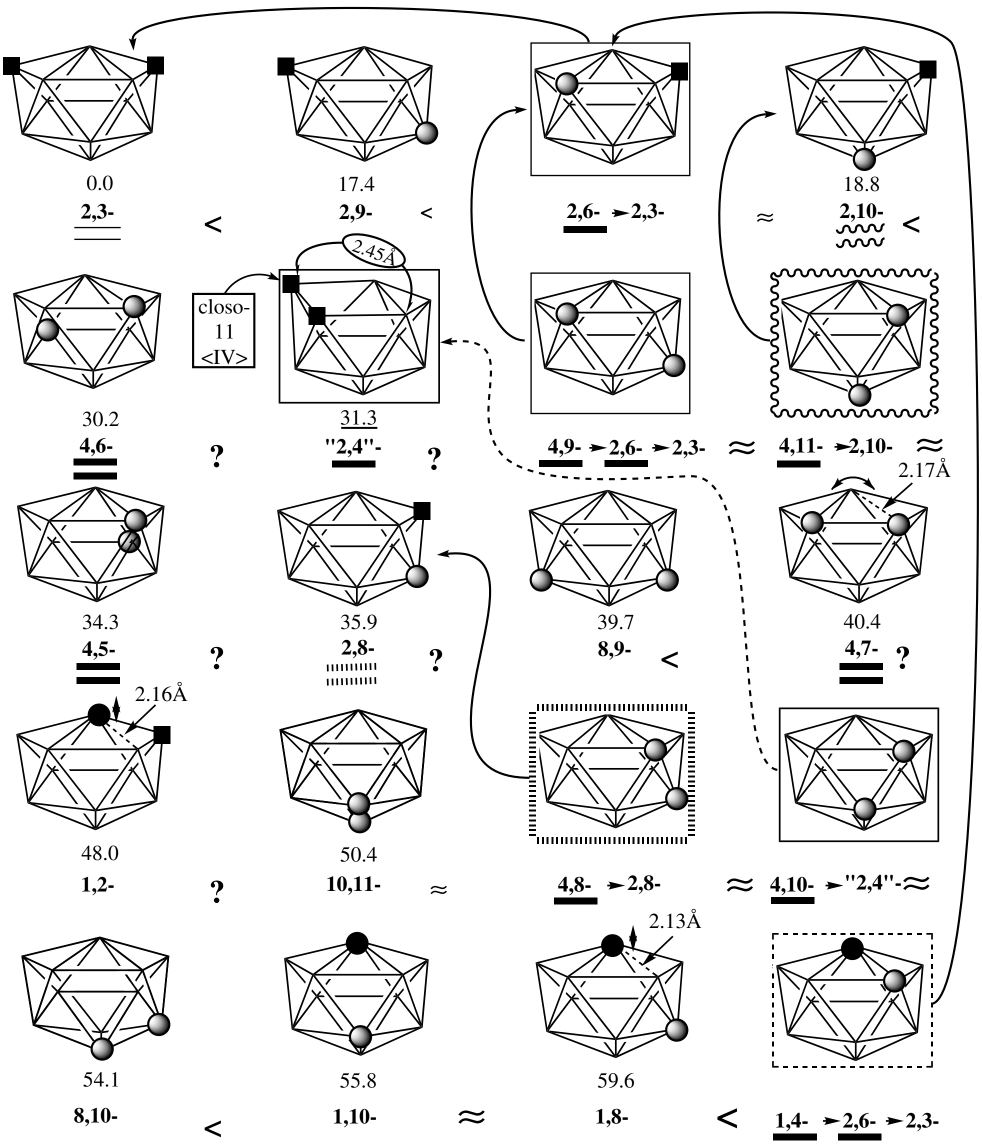

Figure 9. Twenty candidate *closo*-$C_2B_9H_{11}$ carboranes with deltahedral structures reduce to 13.

should be better for carbon than the gunwale 5*k*-positions, which are in a 'bad neighborhood' adjoining the 6*k* position. The 5*k* gunwale-positions may actually be slightly detrimental to the carbon atoms, but, by attracting the skeletal electrons towards the 6*k* site occupied by boron, the 5*k* gunwale-carbon atoms' benefit to the 6*k* boron probably outweighs the detrimental effect on the gunwale-carbon atoms. In any event, the isomers containing two gunwale carbon atoms (4,6-, 4,5- and 4,7-$C_2B_9H_{11}$) are calculated to be 9.1, 5.1, and 15.5 kcal mol^{-1} more stable than estimated. Similar charge-smoothing considerations may also account for the stability of the 1,2-isomer (see Fig. 10).

If our boron-centric concerns about stabilizing 6*k* boron atoms are legitimate, then it suggests that efforts to produce *closo*-carboranes and *closo*-azaboranes, with 13 and more vertices (supraicosahedral deltahedra) and necessarily incorporating multiple 6*k* vertices, may be in peril unless strategies to enrich the 6*k* electronic environments by selected exo-terminal groups can be invented. In this regard, see the elegant investigations by Paetzold *et al.*[7] and Welch[8] in the volume of proceedings arising from the IMEBORON XI conference.

Table 2 summarizes the values generated in Figs 1 to 10 for all eight *closo*-deltahedra. The precise values are listed and averaged with some trepidation. After removing three fringe values (associated with the smallest deltahedra and underlined) the re-averaged values fall into line but still imply more accuracy than is justified from the data. The patterns among the rounded-off energy penalty values merit more attention. It is seen, for example, that breaking one connection in a deltahedral structure (all faces are triangular) to form one square open face engenders about ~10 kcal mol^{-1}

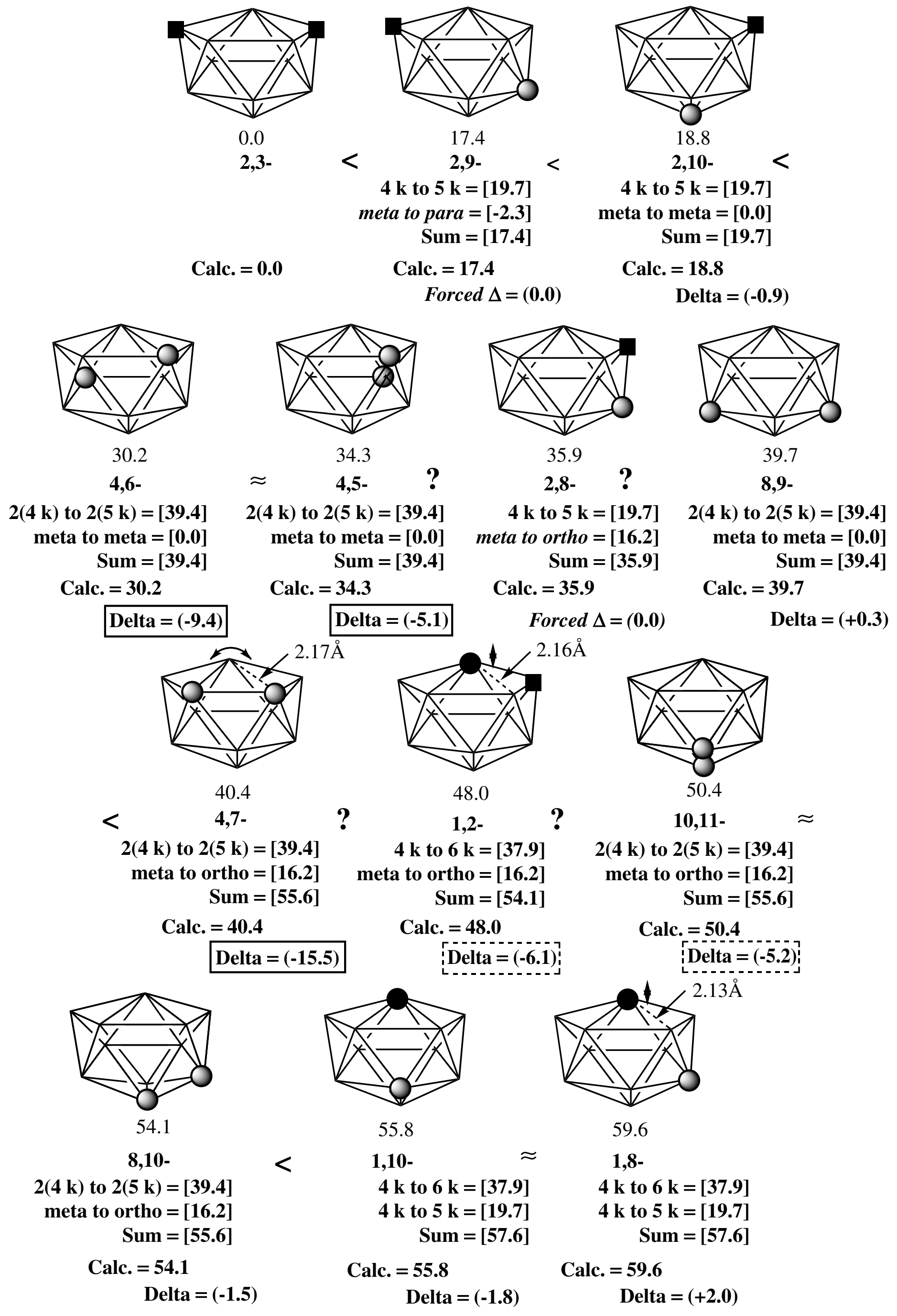

Figure 10. Thirteen surviving *closo*-11<III>, $C_2B_9H_{11}$, isomers.

less stability, but if it gains ~21 kcal mol^{-1} from a 5*k* to 4*k* carbon conversion in the same transition then the overall transaction results in a net gain of ~11 kcal mol^{-1}.

A number of mechanistic questions remain about how some deltahedral *closo*-carborane structures (*closo-n*<III>) rearrange into alternative *closo-n*<III> structures and how and why some deltahedral *closo-n*<III> structures rearrange into alternative *closo-n*<IV> structures with square open faces.

Figure 12 illustrates the pathways by which a sequence of matching DSD rearrangements account for the optimization of five isomers illustrated in Fig. 9 into three more stable isomers. In all five cases, *one* carbon was in a gunwale site prior to rearrangement and after one or two DSD rearrangements there were *zero* carbon atoms in gunwale locations.

Figure 13a illustrates the probable pathway by which a similar DSD rearrangement accounts for the optimization of

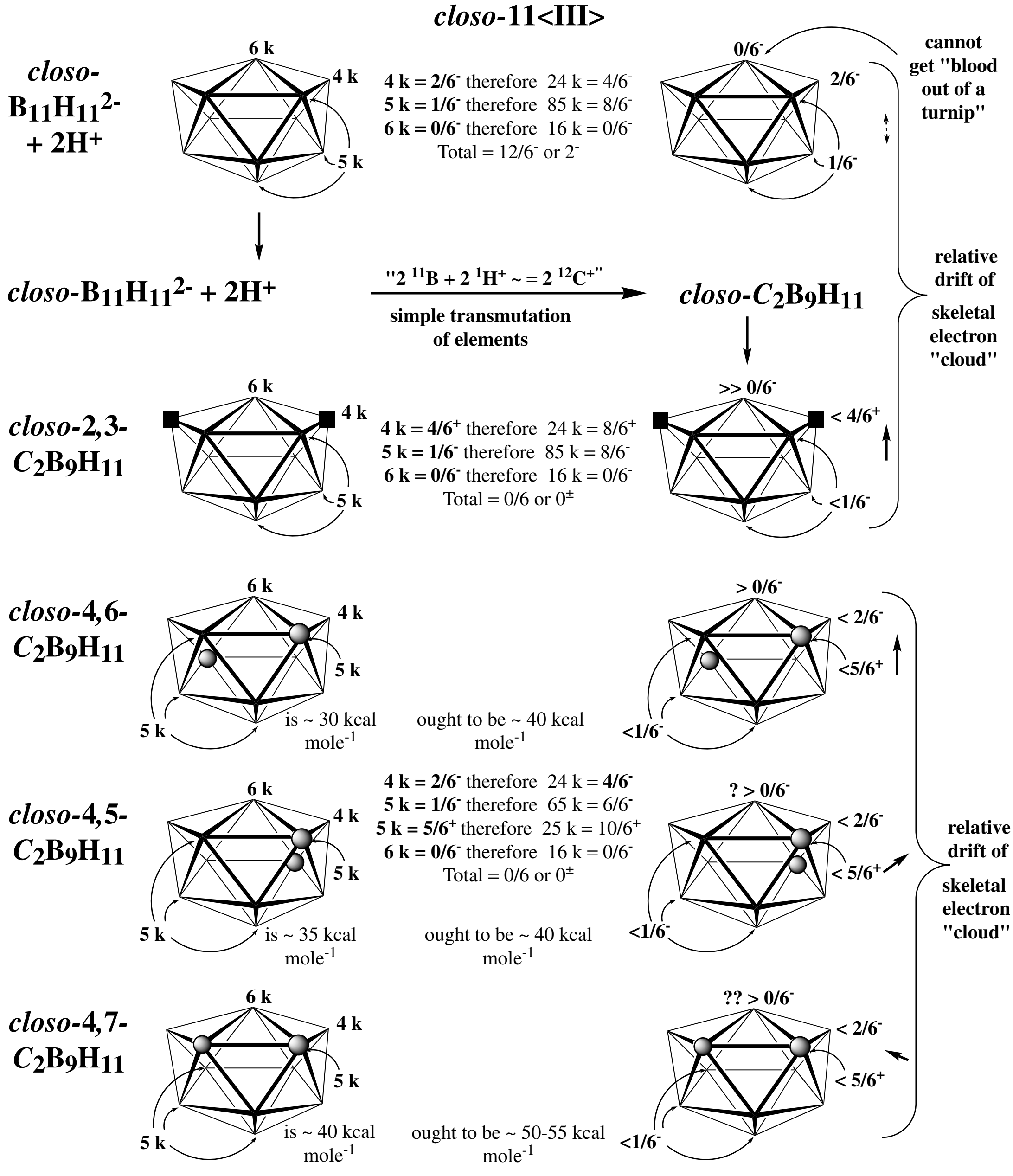

Figure 11. Why some *closo*-11<III> isomers are unexpectedly stable.

the candidate 2,4- and 4,10-isomers into a '2,4'-*closo*-11⟨IV⟩ configuration. In both cases, *one* carbon was in a gunwale site and, after zero or one DSD rearrangement, a final DS rearrangement allows the *closo*-11⟨III⟩ deltahedron, which incorporates one 6*k* vertex, to open into the '2,4'-*closo*-11⟨IV⟩ polyhedron. This deviant *closo*-11⟨IV⟩ structure incorporates two adjacent 4*k*-edges and one 4*k*-cage, and has zero 6*k* and zero gunwale locations. Both carbon atoms occupy the two adjacent 4*k*-edge positions.

It is noteworthy that two adjacent 4*k*-edge positions are also ideal for housing one bridge hydrogen, and indeed Paetzold and co-workers[9] have produced just such a compound. Figure 13b illustrates the conversion of *closo*-$B_{11}H_{11}^{2-}$ (*closo*-11⟨III⟩) into *closo*-$B_{11}H_{12}^{-}$ (*closo*-11⟨IV⟩) by the addition of a proton.

Another discovery is worth noting. The usual 'most spherical' deltahedral *closo*-13⟨III⟩ structure, characteristic of metalla-carboranes, incorporates one 4*k*-cage vertex between *two* 6*k*-cage vertices. Welch and coworkers[10] have revealed the first true *closo*-13-vertex carborane; see Figure 13c. It has a 'surprising' *closo*-13⟨IV⟩ structure that incorporates two adjacent 4*k*-edge locations as well as only one 6*k* location, not *two*. Both carbon atoms occupy the two adjacent 4*k*-edge positions. Perhaps the two 4*k* carbon atoms can stabilize the one

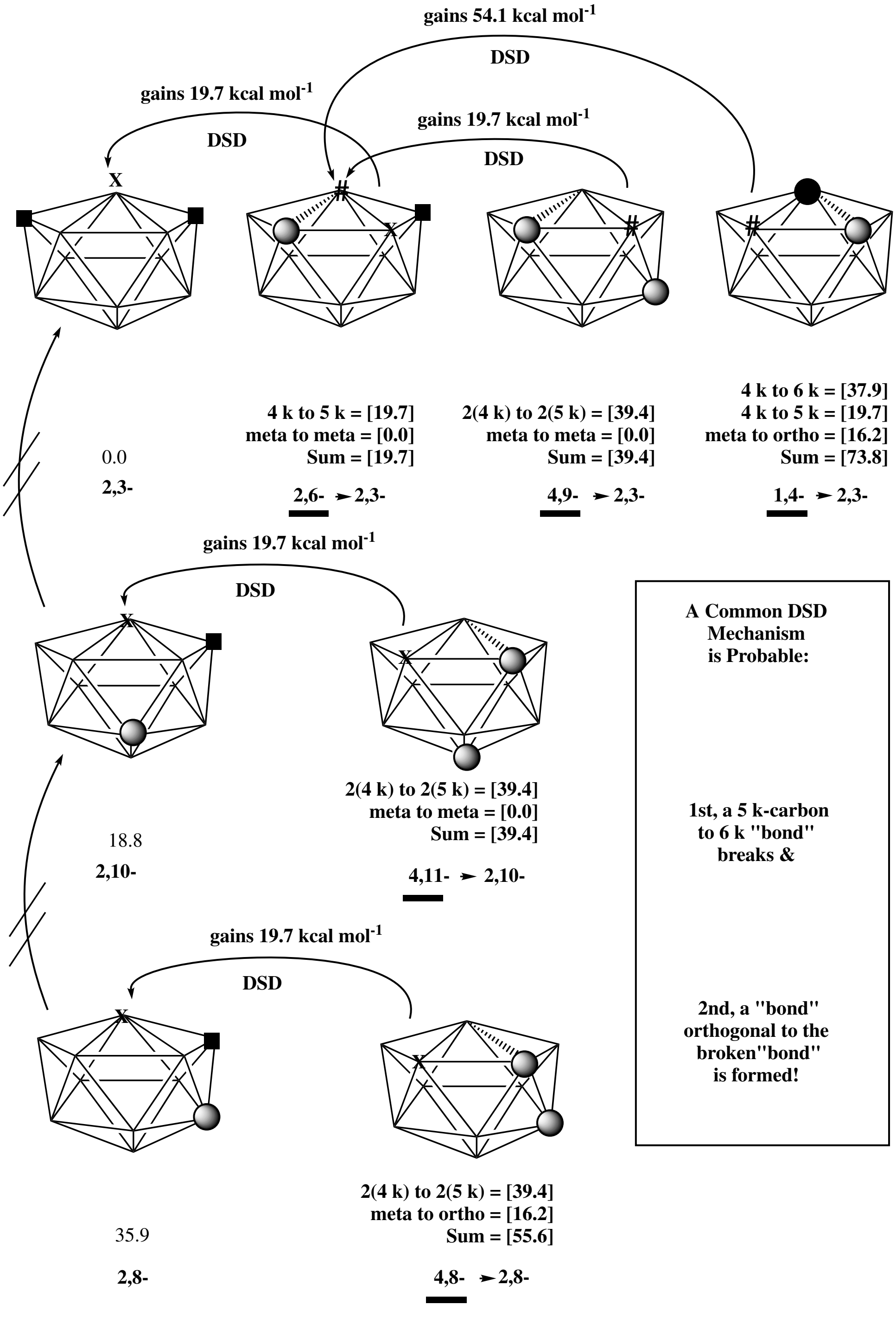

Figure 12. How eight *closo*-$C_2B_9H_{11}$ isomers reduce to three.

6*k* boron in a less favored structure more than adjacent 4*k* and 5*k* carbon atoms can stabilize two 6*k* boron atoms in a more favored configuration. Welch and co-workers are after even larger closo-carboranes, and one wonders whether 6*k* vertices or square open faces will prevail.

It must be more than coincidence that all *seven* mono-gunwale carbon isomers optimize into zero-gunwale carbon alternatives (Figs 12 and 13a) and that, in contrast, all three dual gunwale carbon isomers (Fig. 11) do not rearrange. In Fig. 14, the 4,6-, 4,5- and 4,7-dual gunwale carbon isomers are shown with DSD rearrangements paralleling those illustrated in Figs 12 and 13a. That the 4,7-isomer does not rearrange into the less stable 1,2-isomer is understandable, but that the 4,6- and 4,5-isomers do not optimize into the 2,9- and 2,10-isomers

Table 2. Energy penalties (kcal mol^{-1})

Vertex	3*k* to 4*k*	4*k* to 5*k*	5*k* to 6*k*	4*k* to 6*k*	'para to meta'	'para to ortho'	'meta to ortho'	*closo*-⟨III⟩ to *closo*-⟨IV⟩
5_{3k4k}	24.9						11.6	
6_{4k}							8.3	
7_{4k5k}		30.2					16.6	
8_{4k5k}		23.9					21.9	9.3
9_{4k5k}		20.4					13.6	
10_{4k5k}		20.9			0.4	18.7	**18.3**	
11_{4k5k6k}		19.7		37.9	2.3	**18.5**	16.2	11.6
12_{5k}					2.8	18.8		
Average								
all data	24.9	23.0		37.9	1.83	18.7	15.2	10.45
no outriders	24.9	21.2	16.7 (extrapolated)	37.9	1.83	18.7	17.3	10
Rough energy penalties	25 Δ = 4	21 Δ = 4	17 Δ = 4	38	2	18 is penalty for adjacent carbon atoms		10

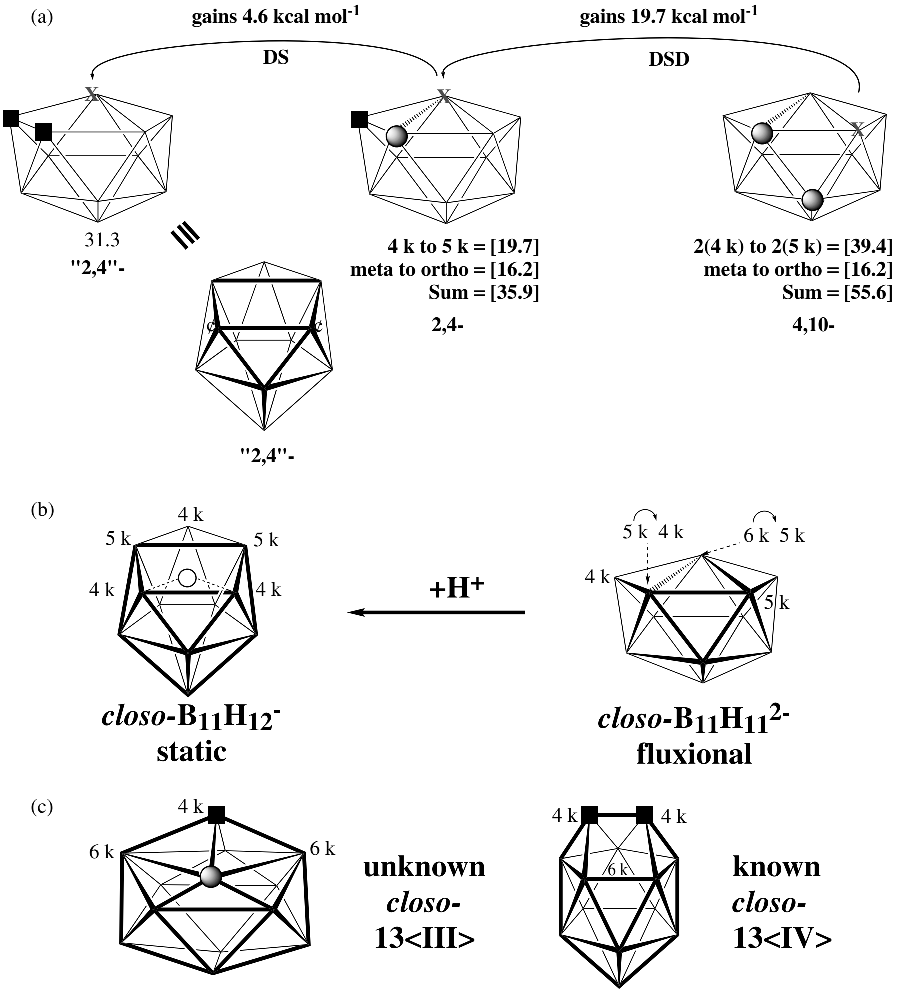

Figure 13. (a) The *closo*-11⟨III⟩ to *closo*-11⟨IV⟩ rearrangements of two potential *closo*-$C_2B_9H_{11}$ isomers. (b) The *closo*-11⟨III⟩ to *closo*-11⟨IV⟩ rearrangement that accompanies conversion of $B_{11}H_{11}^{2-}$ into $B_{11}H_{12}^{-}$. (c) The potential *closo*-13⟨III⟩ and *closo*-13⟨IV⟩ structures of two *closo*-$C_2B_{11}H_{13}$ isomers.

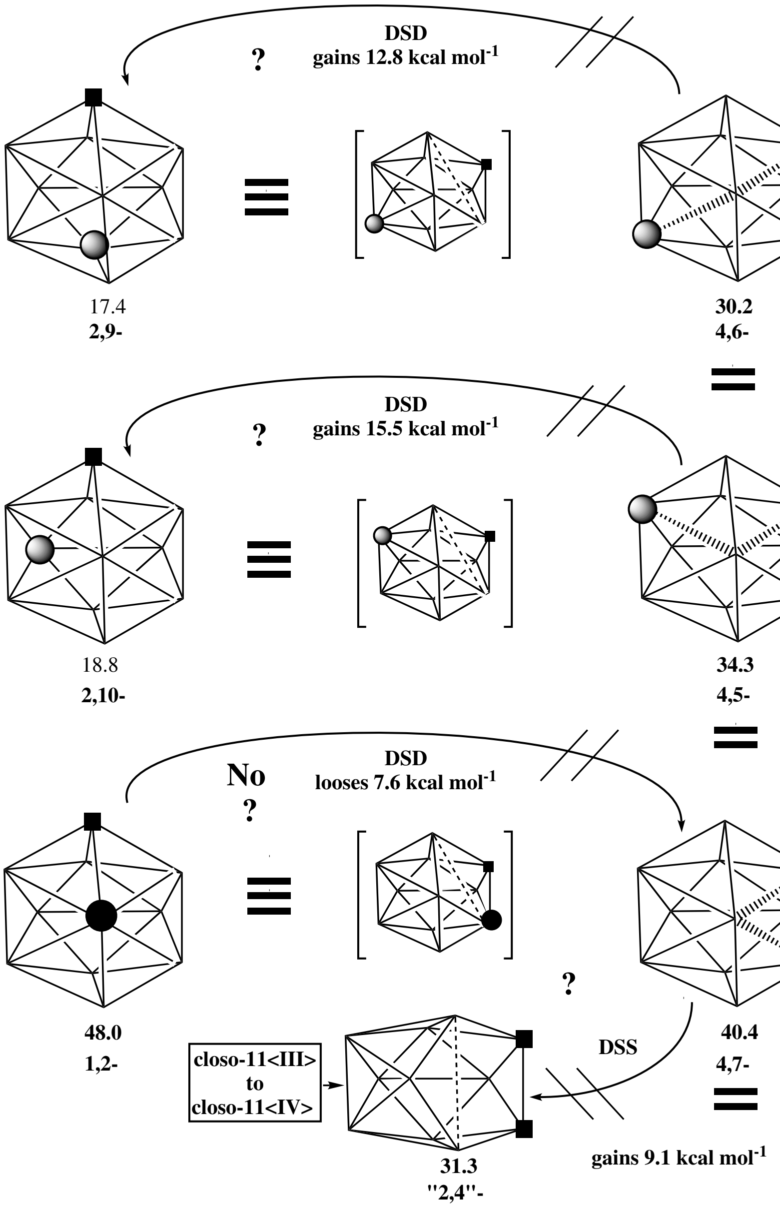

Figure 14. Isomers of *closo*-$C_2B_9H_{11}$ with two carbon atoms in gunwale positions do not rearrange upon optimization.

is mystifying, as they would gain 12.8 kcal mol^{-1} and 15.5 kcal mol^{-1} respectively. One also wonders, reflectively, why the 4,7-isomer does not untether the carbon atoms from the 6*k* boron, 'slightly redistributing' the skeletal electrons, to form the '2,4-' isomer illustrated in Figs 13a and 14 and gain 9 kcal mol^{-1}.

Remember the *closo*-8⟨III⟩ candidate 3,5- and 1,3-$C_2B_6H_8$ isomers in Fig. 5? The 3,5-isomer rearranged into the most stable *closo*-8⟨III⟩ 1,7-structure. The 1,3-isomer rearranged into a *closo*-8⟨IV⟩ structure. In Fig. 15a the *closo*-8⟨IV⟩ structure is renumbered as the 5,6-isomer instead of the '1,3-' isomer in Fig. 5. In a similar fashion, in Fig. 15b the *closo*-8⟨III⟩ 3,5-isomer possibly involves an unstable *closo*-8⟨IV⟩ 5,7-configuration, as it optimizes into the most stable *closo*-8⟨III⟩ 1,7-isomer of $C_2B_6H_8$. Lastly, in Fig. 15c, the scrambling of the boron atoms in the 1,7-*closo*-8⟨III⟩ structure has been reported[11] to take place via the intermediate 3,4-*closo*-8⟨IV⟩. Higher level calculations redefine the 3,4-*closo*-8⟨IV⟩ structure as a transitions state and lower the relative stability value from 1.93 to 1.9 kcal mol^{-1}.

Invoking three different *closo*-8⟨IV⟩ isomers in Fig. 15 invites a comparison of all six possible *closo*-8⟨IV⟩ isomers of $C_2B_6H_8$ incorporating 4*k* carbon atoms only. The carbon-apart isomers (5,7-, 3,4- and 3,7-), at the top of Fig. 16, should be more stable than the carbon-adjacent isomers (5,6-, 3,5- and 5,8-). The two sets are compared with the two related *closo*-8⟨III⟩ isomers to their left.

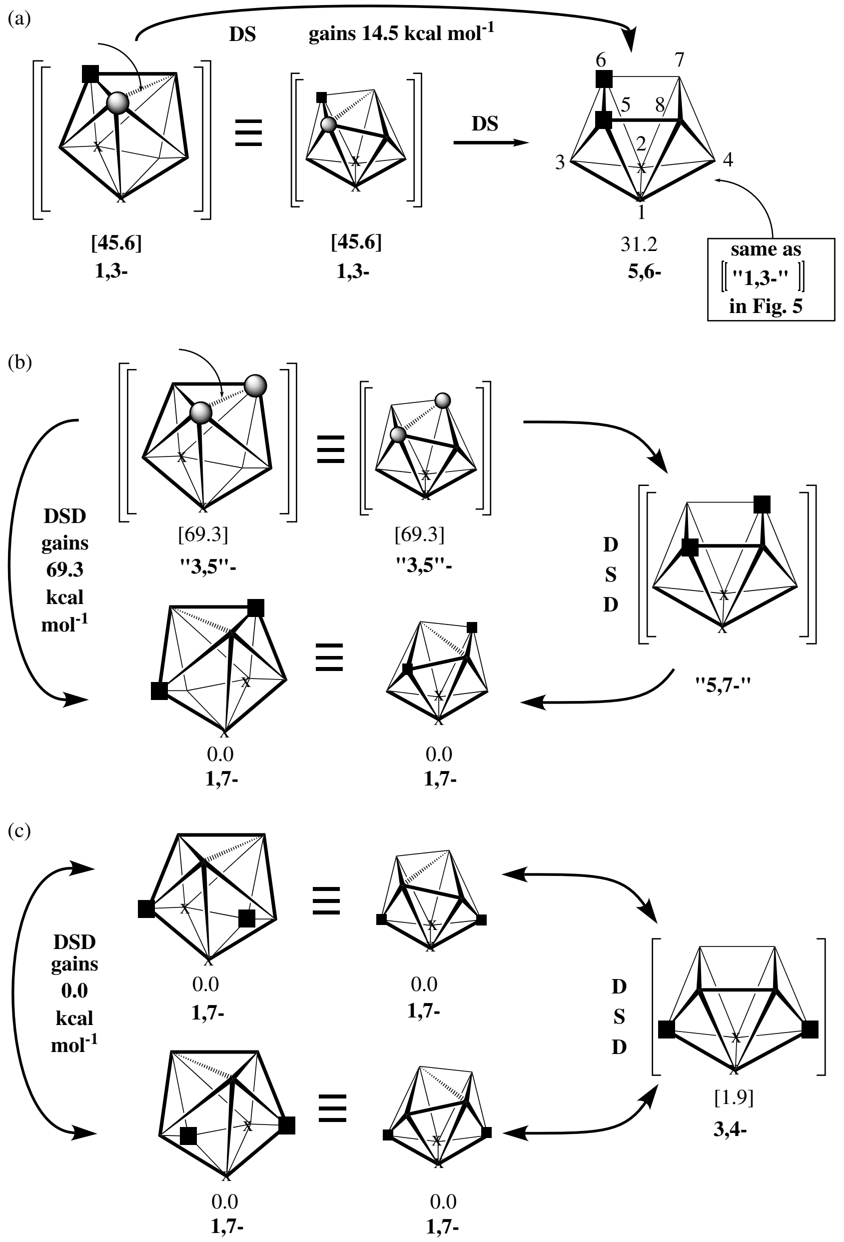

Figure 15. (a) Rearrangement of 1,3-*closo*-$C_2B_6H_8$ (*closo*-8<III>) into 5,6-*closo*-$C_2B_6H_8$ (*closo*-8<IV>) isomer. (b) Rearrangement of 3,5- into 1,7-isomer. (c) The 4 : 2 ^{11}B NMR spectrum in the 1,7-isomer.

Two conflicting arguments jump to mind. The 3,4-⟨IV⟩-isomer[11] has to be involved in making the four boron atoms equivalent in the ^{11}B NMR spectrum of the 1,7-⟨III⟩-isomer and it is only 1.9 kcal mol^{-1} less stable than the 1,7-⟨III⟩-isomer. On the other hand, would the 5,7-⟨IV⟩- and 3,7-⟨IV⟩-isomers be more or less stable than the 3,4-⟨IV⟩-isomer; their opening and closing would not be detected in the ^{11}B NMR spectrum. If the more prevalent 4*k*-edge positions are slightly better than 4*k*-cage positions for carbon, as arguably might be the case, then they might be more stable intermediates but result in nothing observable in the ^{11}B NMR spectrum. Among the carbon-adjacent isomers, the 5,6-⟨IV⟩-isomer is a stable species with the carbon atoms in 4*k*-edge positions and is only 9.3 kcal mol^{-1} less stable than the 1,2-⟨III⟩-isomer; see Fig. 5. Both the 5,6-⟨IV⟩- and 5,8-⟨IV⟩-isomers would not convert into the 1,2-⟨III⟩-isomer in a simple (one-step) fashion. The 3,5-⟨IV⟩-isomer would probably optimize into the 1,2-⟨III⟩-isomer. A transition state ⟨III–IV⟩ '5,8' was found.

Upon recalculation, the ⟨III⟩ 1,5-isomer (Fig. 5) is found to be a transition state that would tend to rearrange spontaneously into the ⟨III⟩ 1,7-isomer. The possible sequence, including the deviant 3,7-configuration (*closo*-8⟨IV⟩), is displayed in Fig. 17.

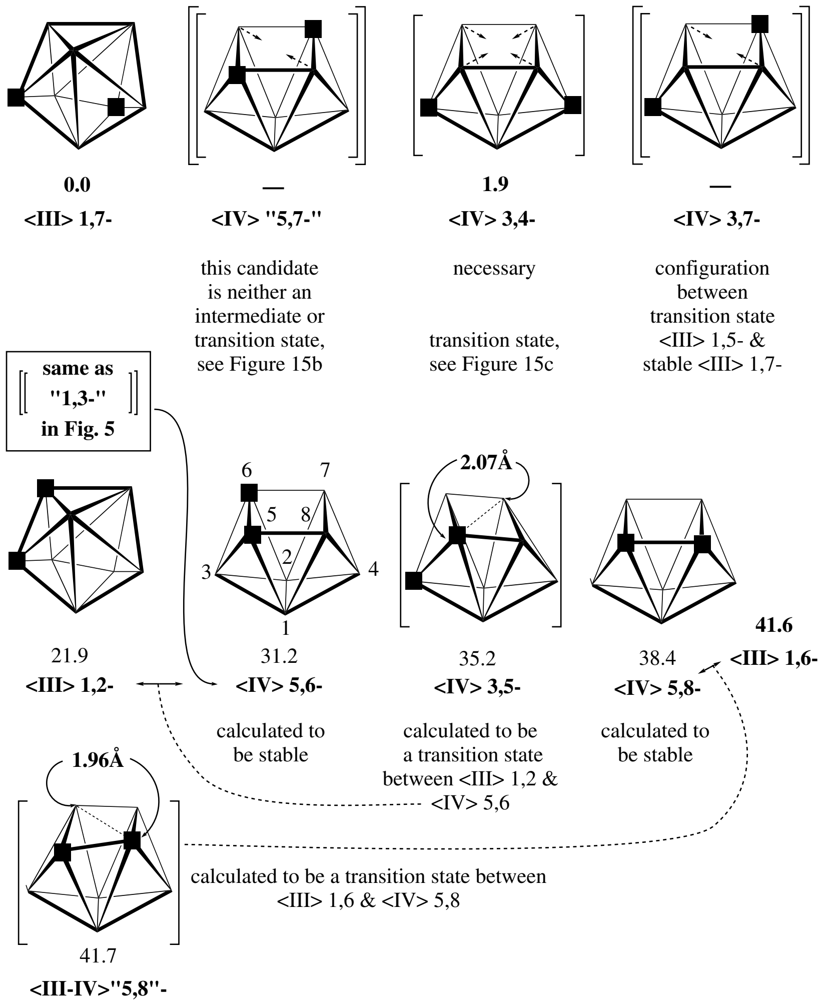

Figure 16. Relative energies of *closo*-$C_2B_6H_8$ *closo*-8⟨IV⟩ and related *closo*-8⟨III⟩ isomers.

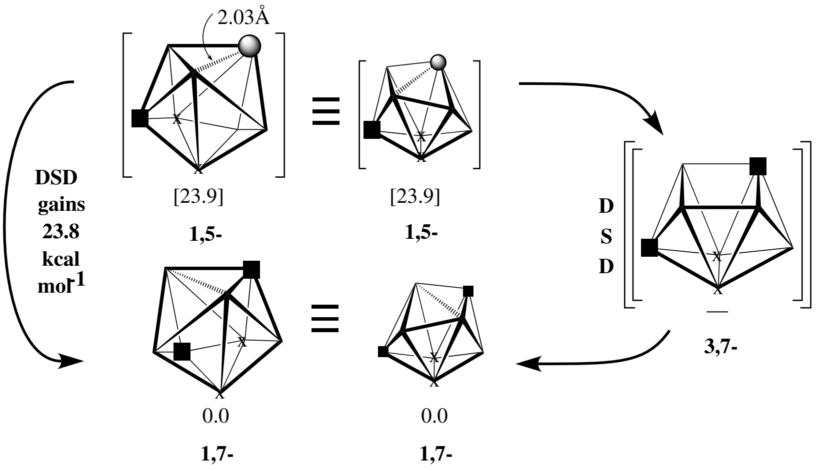

Figure 17. Rearrangement of the 1,5-isomer (a transition state) into the 1,7-isomer through a configuration resembling the 3,7-isomer of *closo*-8⟨IV⟩.

COMPUTATIONAL STUDIES

All *ab initio* calculations were performed employing the Gaussian 94 program.[12] The geometries were fully optimized at the DFT B3LYP/6-311G* level within the specified symmetry constraints on Linux-based PCs. A vibrational frequency analysis was carried out on each optimized geometry to characterize the nature of the stationary point and confirm that a true minimum had been found.

CONCLUSIONS

The original 52 candidate dicarba-*closo*-carborane structures reduce to 42 as seven isomers spontaneously optimize into more stable *closo-n*<III⟩ species ($n = 5$ to 12) and three *closo-n*<III⟩ isomers spontaneously rearranged into a *closo*-8⟨IV⟩ structure and a *closo*-11⟨IV⟩ structure. Both *closo*-8⟨IV⟩ and *closo*-11⟨IV⟩ isomers incorporated adjacent carbon atoms in 4*k*-edge positions in the four-membered open faces in each case.

All but three of the remaining 42 two-carbon *closo*-carboranes fall in line with the 1969 projections, thus confirming the original hypotheses that carbon atoms prefer low-coordination nonadjacent sites.[5,6] For the remaining 39 isomers, the differences, between the calculated and estimated stability values, seldom exceed 6 kcal mol^{-1}.

Among the 20 potential *closo*-11⟨III⟩ isomers of $C_2B_9H_{11}$, all seven isomers that incorporated *one*, and only one, carbon in 'gunwale' positions spontaneously rearranged into alternative structures with *zero* carbon atoms in 'gunwale' positions. Of the remaining 13 isomers, all three isomers that incorporated *both* carbon atoms in 'gunwale' sites did not rearrange and tended to be slightly more stable than estimated. It is suggested that the attraction, by the gunwale-carbon atoms, of the skeletal electrons 'towards' the 6*k*-site may stabilize the boron therein.

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