iron(II) complexes in solution. Therefore, the lattice influence on the dynamics of the HS ⇌ LS equilibrium seems to be less pronounced than the lattice influence on its thermodynamics. Line-broadening effects in the Mössbauer spectra are also observed for other iron(II) complexes.[44] We suppose that in these cases the dynamics of the spin equilibrium becomes detectable within the Mössbauer time scale.

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Registry No. [Fe(2-pic)$_3$](PF$_6$)$_2$, 80105-98-2.

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Theoretical Study of Rearrangements in Boranes

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In the following paper we present the results of a theoretical study of borane and carborane skeletal rearrangements. We show that tensor surface harmonic (TSH) theory is very useful in rationalizing the different energy barriers to rearrangement exhibited by *closo*-boranes and -carboranes. In particular, we are able to explain why the diamond–square–diamond (DSD) process is favored and to compare it with possible alternative mechanisms for $B_5H_5^{2-}$. We show that TSH theory provides a very simple selection rule for distinguishing symmetry-allowed from symmetry-forbidden processes: the latter involve transition states with a single atom on a rotation axis of order 3 or more. We combine this rule with the criterion that rearrangements involving smaller numbers of simultaneous DSD processes are most favorable to consider the relative energy barriers to skeletal rearrangement of the nido boranes and carboranes. Our conclusions are tested by approximate SCF calculation with the Fenske–Hall method, and some of the proposed transition states are investigated by ab initio SCF calculation with STO 4-31G basis sets and the CADPAC package to optimize geometries and evaluate force constants. The results suggest that for $B_8H_8^{2-}$ a single-DSD process leads to a transition state of distorted C_{2v} geometry. For $B_{12}H_{12}^{2-}$ the mechanisms previously proposed in the literature are found to be incorrect.

Introduction

Many years have passed since Alfred Stock synthesized the first boranes,[1] but the field of study that he opened up is still a fruitful one for both inorganic and theoretical chemists. Most theoretical effort has been directed toward an understanding of the electronic structure of boranes and carboranes in their experimentally observed equilibrium geometries,[2–9] and although recent work shows that this subject is by no means exhausted, they are reasonably well-understood. In contrast, the variation in magnitude of the energy barrier to skeletal rearrangements in these species is less well-understood—this is the problem we wish to address.

The diamond–square–diamond mechanism for the skeletal rearrangement of boranes was first proposed by Lipscomb.[10] In this process, illustrated in Figure 1, an edge common to two triangular faces of the cluster skeleton breaks and a new edge is formed perpendicular to it. DSD rearrangements, or combinations of several concerted DSD processes, have been proposed to rationalize fluxional processes and isomerizations of boranes, carboranes, and metallaboranes.[2,11] King[12] has used topological and group-theoretical considerations to distinguish between inherently rigid clusters (which contain no *degenerate* edges) and those for which one or more DSD processes are *geometrically* possible. An edge is said to be degenerate if a DSD rearrangement in which it is broken leads to a product having the same cluster skeleton as the starting material. For example, the three equatorial edges of $B_5H_5^{2-}$ are degenerate and the remainder are not. King's approach was partially successful in that all the structures he predicted to be rigid are found experimentally to be nonfluxional. However, some molecules of the $B_nH_n^{2-}$ series have geometrically allowed rearrangements involving one or more DSD processes but do not show any fluxional behavior.

Calculations at the PRDDO level have shown that $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ both have low-energy geometries corresponding to the postulated single-DSD-mechanism transition states.[13,14] Recently, Gimarc and Ott have used elementary group-theoretical arguments to show that the single-DSD processes which are geometrically allowed in $B_5H_5^{2-}$ and $B_9H_9^{2-}$ are both forbidden by symmetry (in the Woodward–Hoffmann sense) and that there is a symmetry-allowed double-DSD mechanism available for $B_9H_9^{2-}$.[15–17] These results highlight the need for a consistent theory to rationalize the experimentally observed order of fluxionality of *closo*-boranes and the directly related problem of the number of isolable carborane isomers in the $C_2B_{n-2}H_n^{2-}$ series of compounds. This is the subject of the following sections.

A graph-theoretical approach is appealing, owing to its simplicity and ease of interpretation. In particular, it might be

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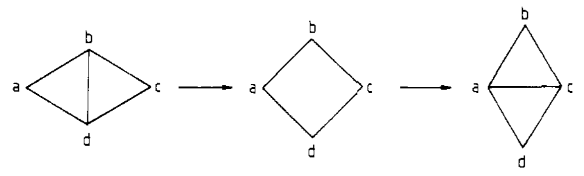

Figure 1. The diamond–square–diamond (DSD) rearrangement.

supposed that the *Hamiltonian path* criterion would enable one to identify favorable transition states. A Hamiltonian path around the edges of a cluster must link all the skeletal vertices without repetition and must begin and end at the same atom. By considering the pairwise interaction of tangential p orbitals on the skeletal atoms along such a path, King and Rouvray have deduced the $n + 1$ skeletal electron pair count for deltahedral boranes.[18] However, the carbon skeleton of prismane has a Hamiltonian path and this molecule certainly does not have $n + 1$ skeletal bonding orbitals. Additional topological considerations that distinguish between edge-localized and globally delocalized clusters resolve this difficulty.[19,20] However, we found that the symmetry-based tensor surface harmonic (TSH) theory[21-25] provided a better framework for this study. The application of this model to borane and carborane rearrangements is detailed in the remaining sections.

Tensor Surface Harmonic Analysis of Skeletal Rearrangements

Tensor surface harmonic (TSH) theory in its simplest form is a method for deducing approximate LCAO–MO wave functions for cluster compounds whose skeletal atoms lie approximately on a spherical surface. The cluster orbitals are derived from the eigenfunctions for a free particle constrained to move on the surface of a sphere, namely the spherical harmonics, and from the related tensor spherical harmonics. The reader is referred elsewhere for details of the theory.[21-25] Since its inception substantial use has been made of the method for the discussion of the electronic structures of cluster compounds,[26-32] and various theoretical studies have also been performed.[33-38]

We have found the method to be useful in the consideration of rearrangements in several ways. The first is concerned with the identification of symmetry-forbidden processes, which are rearrangements exhibiting a crossing of occupied and virtual molecular orbitals. As previous studies have shown,[37] the occupied cluster orbitals of fully deltahedral boranes consist of the even π set and the S^{σ} orbital. (In fact, there is some mixing of functions that transform according to the same irreducible representation of the molecular point group, but this does not affect the symmetries of the set of occupied cluster orbitals.) Hence, the identification of the symmetries of the occupied molecular orbitals is a straightforward matter for both starting material and product. Reduction in symmetry is then performed to the point group containing the symmetry elements retained throughout the process. If the symmetries of the sets of bonding orbitals referred to this point group are not equivalent, then a crossing must occur and the rearrangement will be energetically unfavorable.

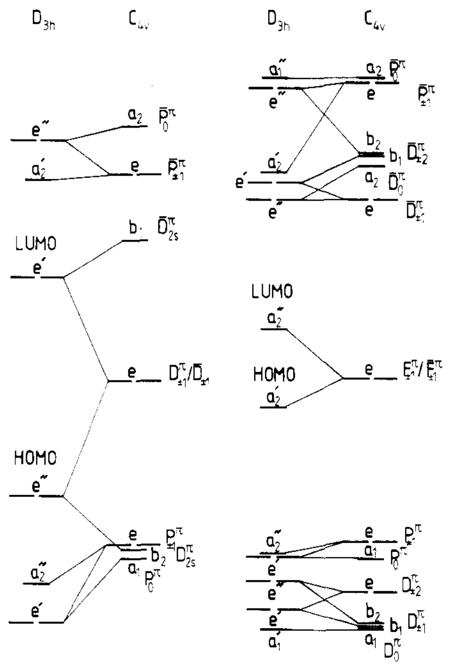

Figure 2. Structural tensor surface harmonic (TSH) correlation diagrams for the single-DSD rearrangements in $B_5H_5^{2-}$ (left) and $B_9H_9^{2-}$ (right). The energy scales and origins are different. TSH labels are also included; for example, $P^{\pi}_{\pm1}$ are the π cluster orbitals with $L = 1$ and $M = \pm1$ and D^{π}_{2s} is the π cluster orbital with expansion function xy.[25]

The HOMO and LUMO of *closo*-borane compounds are usually related by a parity transformation.[21,29] When this is the case, mixing between the HOMO and LUMO is not possible if a plane or center of symmetry is retained throughout the rearrangement. However, we should note that many symmetry-allowed rearrangements will not be favorable: clearly, if no symmetry elements are preserved throughout the process, then there cannot be a crossover, but this is no guarantee that the energy barrier to the process will be small. Further, it is not sufficient merely to consider the behavior of the frontier orbitals for molecules such as these, where a localized description of the bonding is largely inappropriate. Orbitals other than the HOMO and LUMO may also change appreciably in energy, as the correlation diagrams considered later in this section illustrate.

More detailed considerations allow us to deduce a very simple selection rule to identify rearrangements that involve crossings of the above type. *We find that a crossing occurs if the proposed transition state has a single atom lying on a principal rotation axis of order 3 or more.* For a single-DSD process this is the case if the degenerate edge lies opposite a single atom, as it does in $B_5H_5^{2-}$ and $B_9H_9^{2-}$, in agreement with the conclusions of Gimarc and Ott.

The proof of the above theorem is straightforward. The p^{π} orbitals of the unique atom lying on the principal axis will span an E irreducible representation if the molecular point group is axial and the axis is of order 3 or more. Further, it can easily be shown that the total number of E representations in the $L^{\pi}/\bar{L}^{\pi}$ set is then odd,[32] and the TSH pairing principle[24] then implies that one pair must be self-conjugate and nonbonding. In closo systems these frontier orbitals are usually localized mainly on the unique atom,[32] but this need not be the case for transition states with more open structures. However, this does not affect the conclusion that such transition states will have a doubly degenerate, nonbonding pair of E orbitals at the HOMO–LUMO level that correspond to the crossover of two molecular orbitals at this geometry. This is illustrated in Figure 2 for the single-DSD

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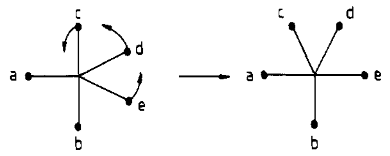

Figure 3. The turnstile rotation mechanism.

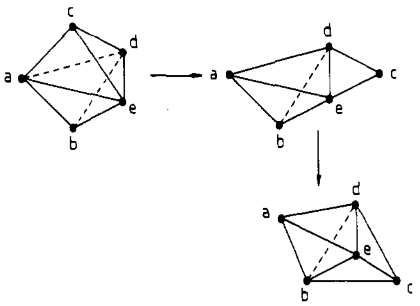

Figure 4. The edge-cleavage mechanism.

processes in $B_5H_5^{2-}$ and $B_9H_9^{2-}$. Only the π cluster orbitals are considered, and the units of energy are parameterized. These diagrams were produced by evaluating the Fock operator matrix elements approximately in a basis set of cluster orbitals and diagonalizing to include the π–π mixing.[25] The matrix elements were assumed to be proportional to the overlap of Slater-type p orbitals centered on the vertices. Energies are relative to $\alpha = 0$, so the energy scales and origins of the two diagrams are different.

The above rule will not necessarily hold if the starting geometry includes a single skeletal atom on the principal rotation axis. The fact that such species are comparatively rare and often have n or $n + 2$ skeletal electron pairs[29] is in agreement with the preceding argument.

Investigation of the Diamond–Square–Diamond Mechanism

In this section we discuss the factors that make DSD-type processes energetically favorable for borane clusters. The partial success of King's analysis, discussed above, leads one to conclude that a necessary condition for a molecule to exhibit fluxionality is the existence of one or more degenerate edges. Below we develop a more precise criterion for determining the relative energy barriers to cluster rearrangements.

First, let us consider the $B_5H_5^{2-}$ molecule, which, as we have already seen, has no symmetry-allowed DSD rearrangement. However, one might consider various other possible mechanisms that lead to interchange of the skeletal atoms. The single-DSD process is analogous to the Berry pseudorotation mechanism proposed for ligand rearrangements in PCl_5.[39] Another possibility proposed for this molecule is the turnstile rearrangement[40,41] illustrated in Figure 3. This leads to a transition state with a single plane of symmetry through the unique atom which remains equatorial (d), and we have found by inspection that various other rearrangements of the vertices also give rise to such a geometry. We therefore attempted to optimize this geometry for $B_5H_5^{2-}$ using the CADPAC package[42,43] and a 4-31G basis set. The optimization did not converge well, and a force constant calculation at the final geometry revealed a number of normal modes with negative force constants. Hence, we were unable to locate a transition state of this symmetry. Group-theoretical considerations of the potential surface lead to the conclusion that at every point along the reaction path the reaction coordinate must coincide with one of the normal modes at that point.[44] The motion illustrated in Figure 3 is not along a normal coordinate; symmetry analysis shows that it is a mixture of modes of different symmetry. This supports the ab initio conclusion that it does not describe a possible reaction path.

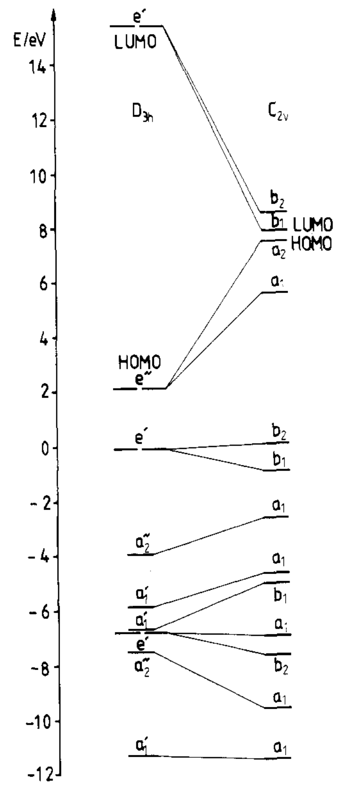

Figure 5. Fenske–Hall correlation diagram for the edge-cleavage mechanism in $B_5H_5^{2-}$.

Johnson's edge-cleavage mechanism[45] (see Figure 4) was also investigated for this molecule. The postulated transition state has C_{2v} symmetry with a single atom on the twofold principal rotation axis, but in this case the symmetry does not require the HOMO and LUMO to be degenerate. In fact $B_{11}H_{11}^{2-}$ and the hypothetical $B_{13}H_{13}^{2-}$ molecule (which has been predicted to be stable[29]) both have a unique atom on the principal twofold rotation axis. In these cases the HOMO and LUMO are widely separated in energy owing to the detailed geometry of the molecules. Experimental evidence[46] suggests that the HOMO–LUMO splitting may also be increased by the presence of substituents on the border atoms of a face that opens during a rearrangement. This is in agreement with our Fenske–Hall calculations on candidate transition states, which show that the HOMO and LUMO may have significant amplitude around an open face. A theoretical analysis of nido and arachno clusters leads to the same result.[23] All substituents are found to increase the rate of the rearrangement: the effect of a Cl substituent is found to be significantly greater than that of a methyl group, as expected from the greater π-donor strength of Cl relative to the π-donor or -acceptor strength of the methyl group.

The $B_5H_5^{2-}$ C_{2v} geometry was studied by approximate SCF calculation using the Fenske–Hall method.[47-50] The resulting correlation diagram is shown in Figure 5. Although there is no crossing of orbitals in this process, we find that the HOMO and LUMO are very close in energy, in contrast to the case of $B_{11}H_{11}^{2-}$. Clearly we would expect this process to have a prohibitively high activation energy. Hence, in discussing lower symmetry species, we must consider the HOMO–LUMO splitting due to the detailed molecular geometry.

Our attempts to find a concerted mechanism alternative to the single-DSD rearrangement for $B_5H_5^{2-}$ were therefore unsuccessful.

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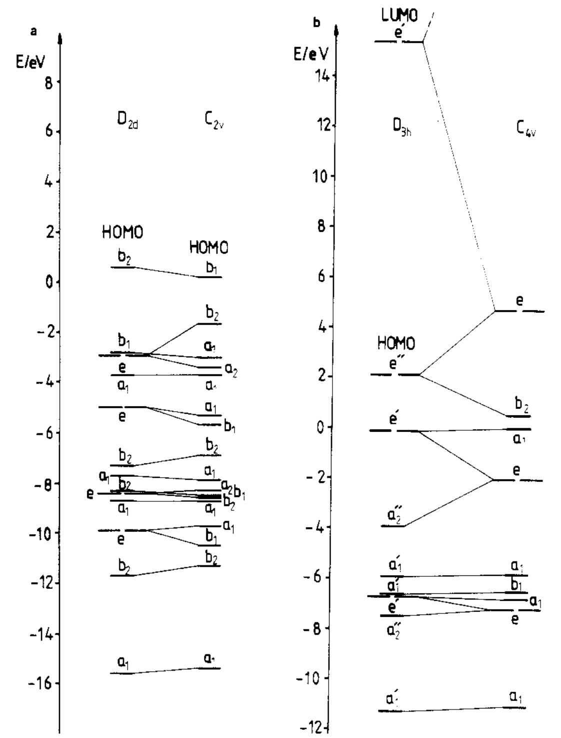

Figure 6. (a) Fenske–Hall correlation diagram for the $B_8H_8^{2-}$ single-DSD process. The LUMO's lie at 11.59 and 7.78 eV for the D_{2d} and C_{2v} geometries, respectively. (b) Fenske–Hall correlation diagram for the $B_5H_5^{2-}$ single-DSD process.

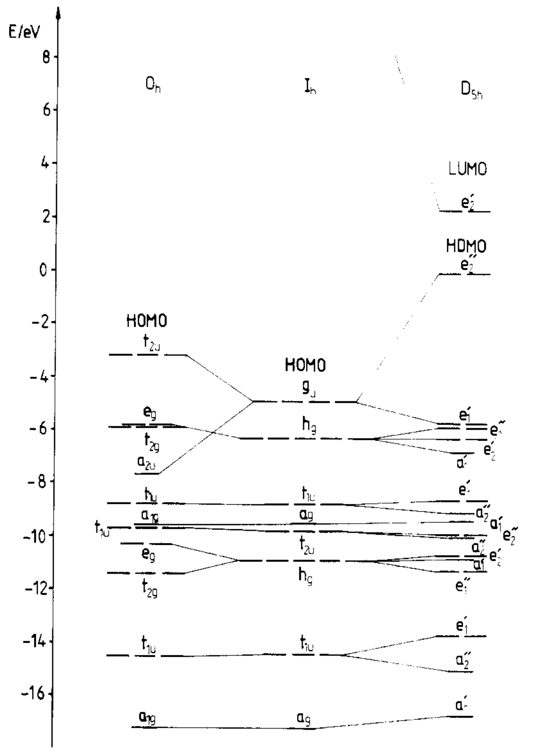

Figure 7. Fenske–Hall correlation diagrams for the $B_{12}H_{12}^{2-}$ sextuple DSD (left) and quintuple DSD (right). The LUMO's lie at 10.83 and 22.01 eV for the O_h and I_h geometries, respectively.

This result is in accord with the available experimental evidence for the lack of $B_5H_5^{2-}$ fluxionality, although it should be noted that only the 1,5-isomer of $C_2B_3H_5$ has been prepared in unsubstituted form.[51] A qualitative understanding of the favorability of the DSD process is not hard to reach, since this mechanism requires a relatively small displacement of the nuclear geometry.[52,53] TSH theory allows us to understand in general terms why this should lead to a low-energy rearrangement. A basic postulate of TSH in its original form[21] is that the detailed arrangement of the skeletal atoms in a roughly spherical cluster is not of primary concern. Later studies have investigated the implications of this assumption and found that many of the results of the original theory still hold true when the structure is explicitly considered.[25,37] In particular, we have shown that the proportionality of the diagonal Fock matrix elements to coordination number is approximately preserved. In a DSD rearrangement the displacement of the skeletal atoms from the starting geometry to the transition state is fairly small, and the change in coordination that occurs is merely a consequence of the opening and closing up of the diagonals of the square face. Hence, we would certainly expect this mechanism to be particularly favorable.

Although we have seen that the DSD mechanism should often give rise to low-energy transition-state geometries, it is also true that such a rearrangement will, in general, be accompanied by a rise in energy. Hence, the larger the number of DSD processes that occur, the greater the increase in energy is likely to be. We therefore deduce the following principle for rationalizing the relative energy barriers of boranes and carboranes to vertex rearrangements: *the smaller the number of simultaneous DSD processes occurring in a symmetry-allowed rearrangement, the more favorable it will be.* This criterion is in good agreement with experimental results and with the conclusions of Gimarc and Ott. The boranes of the series $B_nH_n^{2-}$ with $n = 6$ and 10 have no geometrically possible low-order DSD process available to them, and they are not fluxional on the NMR time scale. For $n = 7$ the lowest order double-DSD process passes through a C_{2v} geometry with an odd atom on the principal axis.[46] Calculation again indicates a high-energy barrier to this process, and $B_7H_7^{2-}$ is also nonfluxional on the NMR time scale. For all three species more than one carborane isomer is known; for $n = 6$ there are two,[54–56] for $n = 7$ there are also two,[57–59] and for $n = 10$ there are three.[60–62] Both $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ have symmetry-allowed single-DSD processes, and both exhibit fluxionality on the NMR time scale.[53,63,64] Only one carborane isomer has been prepared in each case,[51,65–67] although in the case of $C_2B_9H_{11}$ this conclusion is based on NMR evidence alone. Figure 6a shows the correlation diagram for the single-DSD process in $B_8H_8^{2-}$, calculated by using the Fenske–Hall method; there is evidently no significant barrier. For comparison the correlation diagram for the $B_5H_5^{2-}$ single-DSD process calculated by the same method is given in Figure 6b.

The case of $B_5H_5^{2-}$ has been discussed above, while for $B_9H_9^{2-}$ there is no evidence of fluxionality on the NMR time scale.[53] However, only one of the six possible carborane isomers $C_2B_7H_9$

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has been isolated.[68] This geometry represents an intermediate case since there is no symmetry-allowed single-DSD rearrangment, but there is an allowed double-DSD process. Hence, we would expect these molecules to have larger energy barriers to vertex rearrangement than their $n = 8$ and $n = 11$ counterparts but smaller than any of the others.

The case of $B_{12}H_{12}^{2-}$ and the related carboranes $C_2B_{10}H_{12}$ is also interesting. All three carboranes are known; the 1,2-isomer may be converted to the 1,7-species by heating to 470 °C, and the 1,7-isomer may be converted to the 1,12-species by heating to 630 °C. A sextuple-DSD mechanism has been proposed to account for the first interconversion and a relative rotation of layers, which is actually equivalent to a quintuple DSD, for the second.[2] Both processes involve several DSD rearrangements and are therefore expected to be less favorable than the single DSD possible for $n = 8$ and $n = 11$ and the double DSD possible for $n = 9$. Correlation diagrams calculated by using the Fenske–Hall method are given for the $B_{12}H_{12}^{2-}$ sextuple- and quintuple-DSD processes in Figure 7. The geometries used in these calculations are not optimized, but a substantial increase in the HOMO energy is apparent in both "transition states". We discuss these processes further in the next section, where we shall see that these are not in fact transition states at all.

We now apply our theoretical criteria to the *nido*-boranes and -carboranes and predict the relative energy barriers to skeletal rearrangements in these species. The 7- and 8-vertex nido geometries have symmetry-allowed single-DSD rearrangements, both described as 54(43) in King's notation.[12] The 9-vertex nido geometry has a symmetry-allowed double-DSD rearrangement that is equivalent to concurrent 54(53) and 54(44) processes in which the two open faces share an edge. The 10- and 11-vertex nido geometries have no low-order geometrically allowed DSD processes available and are therefore expected to have larger barriers to rearrangement. However, the quintuple DSD that is geometrically possible for the 11-vertex system is not symmetry-forbidden because both starting material and transition state have a single atom on the principal axis. Our prediction for the relative order of the energy barriers of these *nido*-boranes and the corresponding carboranes to skeletal rearrangements is therefore

$$\text{7,8-vertex nido} < \text{9-vertex nido} \ll \text{10,11-vertex nido}$$

Results of Accurate ab Initio Calculation

Some much larger calculations were also performed on candidate transition states for $B_8H_8^{2-}$ and $B_{12}H_{12}^{2-}$ geometries. For comparison we note that the Fenske–Hall calculation on the $B_8H_8^{2-}$ single-DSD transition state required about 20 s of CPU time on an IBM 3081, while the results reported in this section for the same species required about 1 h of CPU time on a CRAY-1S. The CADPAC package was used,[42,43] and 4-31G basis sets were employed throughout. The $B_8H_8^{2-}$ geometries of symmetry D_{2d}, C_{2v}, and D_{4d} were optimized; these correspond to the experimental equilibrium geometry and possible transition-state geometries for single- and double-DSD rearranagements, respectively. The force constants of the two possible transition states were also evaluated by using analytic second derivatives. A major problem with calculations on transition states is that they often exhibit little symmetry.[44,69-72] However, if the geometry is not constrained to be symmetrical, then the computational effort becomes considerably greater. Further, there is the likelihood of collapse into the equilibrium geometry when optimization is attempted unless the point group symmetry is fixed. Unfortunately, such a constraint may mean that the true transition-state geometry cannot easily be reached, as we find below.

The single-DSD C_{2v} geometry was found to have two negative force constants of magnitude 370 and 140 cm^{-1}. The corresponding normal modes are found to resemble the idealized DSD mechanism and a rotation, respectively, and the former is sketched in Figure 8. All three rotational modes were found to have force constants with absolute values of order 100 cm^{-1}, which means that this optimized geometry does not represent a true stationary point.[73] This result indicates that the transition state probably has a geometry which is somewhat distorted from the idealized C_{2v} symmetry used. Such distortion may be related to the effects of border atoms discussed previously in that a greater HOMO–LUMO separation probably results from the lowering of symmetry. The difference in energy between the C_{2v} and D_{2d} optimized geometries is about 70 kJ mol^{-1}. However, this is not necessarily a reliable value because the correlation energies for the two structures may be significantly different.

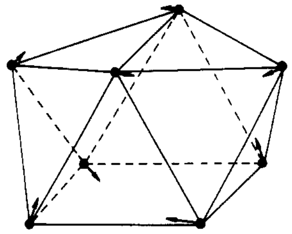

Figure 8. The $B_8H_8^{2-}$ C_{2v} optimized geometry normal mode corresponding to the DSD mechanism.

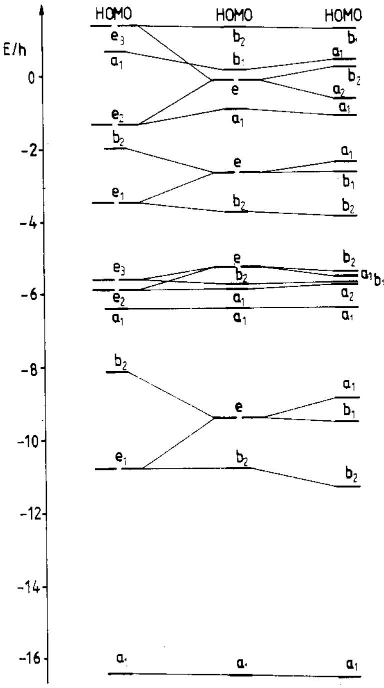

Figure 9. Ab initio correlation diagrams for the $B_8H_8^{2-}$ optimized D_{4d} (left), D_{2d} (center), and C_{2v} (right) geometries. The LUMO's lie at 12.36, 13.15, and 12.13 eV, respectively.

For the square-antiprismatic D_{4d} geometry corresponding to the double-DSD transformation two degenerate normal modes are found to have negative force constants, while the rotational and translational modes have force constants closely approaching the idealized value of zero. As Murrell and Laidler have pointed out,[73] a true transition state must have precisely one normal mode with a negative force constant. If there is more than one such mode, then there must be a pathway of lower energy from reactants to products. The reason for this is easily seen on considering the potential surface for the variation of energy with the two degenerate normal modes, Q_1 and Q_2. The negative force constant means that the second derivative of the energy with respect to each normal coordinate is negative, so that the energy decreases with displacement in either sense along both the Q_1 and

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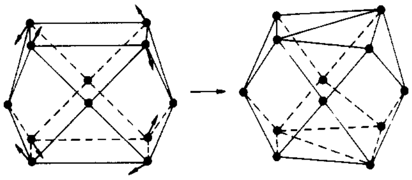

Figure 10. One of the threefold degenerate modes of O_h $B_{12}H_{12}^{2-}$ and the extrapolated D_{2d} geometry to which it leads.

the Q_2 axes. Clearly, this means that lower energy pathways exist, and we found a linear combination of the degenerate modes leading towards the C_{2v} idealized geometry discussed above for the single-DSD process. Correlation diagrams for the optimized geometries are given in Figure 9; we found that the D_{4d} optimized geometry lay 110 kJ mol^{-1} above the D_{2d} and 40 kJ mol^{-1} above the C_{2v}. Comparison with the Fenske–Hall calculations for the single-DSD process shows that the approximate method is in reasonable agreement with the ab initio results, a feature we have noted previously.[25]

For $B_{12}H_{12}^{2-}$ we initially carried out calculations on the I_h, O_h, and D_{5h} geometries corresponding to the equilibrium structure, the proposed sextuple-DSD transition state, and the proposed quintuple-DSD transition state. Force constant calculations for the cuboctahedral geometry (O_h) revealed four negative force constants, three of which are degenerate and smaller in magnitude than the fourth. When these modes are sketched, we find that the largest in magnitude corresponds closely to the postulated sextuple-DSD rearrangement; the other three lead to structures with two pairs of opposite open faces, with the remaining pair of open faces in the O_h geometry closed up across opposite diagonals (Figure 10). Hence, we conclude that the cuboctahedral geometry does not correspond to a true transition state and that the process is likely to be less cooperative than previously supposed.

The D_{2d} geometry suggested by the degenerate modes can be reached from the icosahedral equilibrium geometry by a single-DSD rearrangement that is apparently almost complete and induces the later opening up of four surrounding square faces to accommodate the newly formed bond. From here the system may proceed to the product via a single-DSD rearrangement opposite the newly formed bond. This mechanism involves fewer open faces at any given point along the reaction path and is found to be more energetically favorable than the fully concerted process by about 130 kJ mol^{-1}. However, further calculation reveals that the optimized D_{2d} geometry has three normal modes with negative force constants. Sketches of these modes were again found to give useful insight. In the mode with the negative force constant of greatest magnitude two opposite open faces close up along the equator, while one of the faces that closes in Figure 11 starts to open. In the other two degenerate negative modes one of the open faces closes up along the equator. Hence, the true transition state probably has lower symmetry and fewer open faces than the D_{2d} geometry. One possibility is a C_{2v} structure with two opposite vertices of coordination number 4 and 6 lying on the principal axis; this has only two open faces.

The quintuple-DSD rearrangement has been proposed[2] to account for the conversion of the $C_2B_{10}H_{12}$ carborane 1,7-isomer to the 1,12-species (the sextuple DSD and its modification, above, cannot do this). The optimized D_{5h} geometry was found to have six negative force constants, including the three rotational modes. We therefore conclude that this geometry does not represent a true transition state, although the negative mode of greatest magnitude does correspond to the idealized quintuple-DSD mechanism. In view of the higher energy expected for geometries involving many open faces, we suggest the alternative scheme shown in Figure 11, which has no more than three completely open square faces at any point on the reaction path. Optimization and force constant analysis for the intermediate geometry suggested by this process was not attempted owing to the low symmetry involved.

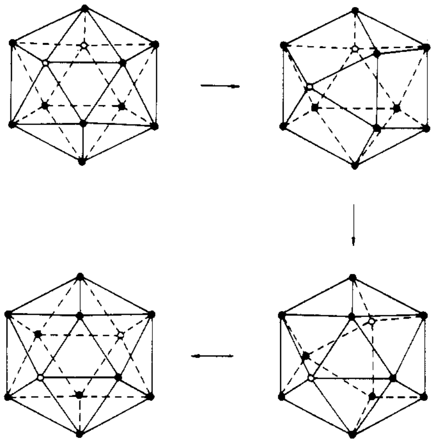

Figure 11. Alternative to the quintuple-DSD $B_{12}H_{12}^{2-}$ scheme.

Both the Fenske–Hall and ab initio calculations that we have performed for the different $B_{12}H_{12}^{2-}$ geometries discussed above show that the energy barriers involved in each case are significantly greater than that for the $B_8H_8^{2-}$ single-DSD rearrangement. For example, the energy differences between the optimized O_h and D_{5h} geometries and the optimized I_h geometry are found to be 680 and 940 kJ mol^{-1}, respectively. We argued above the multiple-DSD processes will generally have higher energy barriers than single-DSD rearrangements. These results confirm this view but also show that a linear dependence of the energy barrier upon the number of open faces should not be expected.

Conclusions

Tensor surface harmonic theory has been used to analyze the skeletal rearrangements of boranes and carboranes. We have shown how this method provides a simple selection rule for the identification of symmetry-forbidden processes and provides a criterion for understanding the energy barriers of symmetry-allowed processes. We have applied the theory to the *nido*-boranes and -carboranes and predicted the relative tendency of these molecules to undergo skeletal rearrangements. Calculations have been performed by using both the Fenske–Hall method and ab initio SCF calculation with 4-31G basis sets. By evaluating the force constants of proposed transition states, we are able to determine how closely they represent the pathway of lowest energy, if at all. We conclude that the single-DSD transition state for $B_8H_8^{2-}$ is likely to have distorted C_{2v} geometry, while studies of the proposed transition states for $B_{12}H_{12}^{2-}$ show that modifications of the mechanisms suggested in the literature are required.

Acknowledgment. We are grateful to Brian Johnson and Alison Rodger for their comments on the manuscript. David Wales thanks the SERC for financial support. We also wish to put on record that Mingos and Johnston independently derived some of the above results.[74]

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