22 July 1966, Volume 153, Number 3734 **SCIENCE**

Framework Rearrangement in Boranes and Carboranes

Cooperative atomic rearrangements are expected in many polyhedron-like electron-deficient molecules and ions.

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The discovery reported in 1934 by Pauling and Weinbaum (*1*) of the B_6 octahedron (joined to other octahedra) in the crystal structure of CaB_6 (Fig. 1) is the beginning of our knowledge of boron polyhedra. The second indication of a polyhedral unit is the icosahedral B_{12} unit in the $B_{12}C_3$ crystal structure, reported by Zhdanov and Sevast'yanov (*2*) in 1941. Although Stock (*3*) had characterized B_2H_6, B_4H_{10}, B_5H_9, B_6H_{10}, and $B_{10}H_{14}$ before 1933, their relation to polyhedral fragments did not begin to become apparent until after the spectroscopic studies of Stitt (*4*) and Price (*5*) on B_2H_6, the crystallographic study by Kasper, Lucht, and Harker (*6*) on $B_{10}H_{14}$, and the proof of the pentagonal pyramidal structure of B_5H_9 by Hedberg, Jones, and Schomaker (*7*) who used the electron diffraction method and by Dulmage and Lipscomb (*8*) who used the x-ray method.

The three-center bonding of bridge hydrogen to two boron atoms was first noted by Longuet-Higgins (*9*), was described as half-bonds by Rundle (*10*), and was rediscovered and generalized to include three-center boron-boron-boron bonds by Eberhardt, Crawford, and Lipscomb (*11*) after low-temperature crystallographic studies of B_5H_9 (*8*), B_4H_{10} (*12*), and B_5H_{11} (*13*). It was also in this attempt (*11*) at a general theory of boron hydrides that framework molecular orbitals in polyhedral B_4Cl_4, $B_6H_6^{-2}$, and $B_{12}H_{12}^{-2}$ were studied. At about the same time Duffy (*14*) gave a valence interpretation of the x-ray results (*15*) on B_4Cl_4, and Longuet-Higgins and Roberts (*16*) discussed rather completely the B_6 octahedron in CaB_6 and the B_{12} icosahedron in $B_{12}C_3$. The major results—that B_4Cl_4 is neutral, but that $B_6H_6^{-2}$ and $B_{12}H_{12}^{-2}$ had to be negative ions—led to confidence in the molecular-orbital method for studies of the ground-state electronic structures of these types of molecules and ions, especially those having high symmetry. Although tetrahedral B_4Cl_4 was known (*15*) at that time, the icosahedral $B_{12}H_{12}^{-2}$ ion (*17, 18*) was not prepared until 1960, and the octahedral $B_6H_6^{-2}$ ion (*19*), not until 1964. In addition I had infered the D_{4d} structure (*20*) of $B_{10}H_{10}^{-2}$ in 1959 from its nuclear magnetic resonance spectrum. The polyhedral B_8Cl_8 structure (*21*) of D_{2d} symmetry was discovered also in 1959. Trigonal bipyramidal $B_5H_5^{-2}$ ion, predicted (*22*) in 1961, has not yet been found but the isoelectronic $C_2B_3H_5$ was subsequently reported.

Isoelectronic sequences form a substantial part of boron chemistry, especially from Stock's work on "inorganic benzene," the borazole molecule $B_3N_3H_6$. But three-dimensional aromatic-like molecules also exist. Stock and Kuss (*23*) noted that aromatic-like compounds result from pyrolysis of acetylene and B_2H_6 or B_4H_{10}. Later, by the time of the report of the preparation by Keilin of one isomer (mentioned in *24*) of $B_3C_2H_5$ (carbon atoms on the threefold axis) and both isomers (*25*) of $B_4C_2H_6$, the valence theory had been extended (*26*) to these compounds. Also, from molecular orbitals, predictions of relative stabilities had been made (*27*), and the structure and most stable isomer (*28, 29*) of $B_5C_2H_7$ correctly inferred. But the widest interest was centered on the three isomers of icosahedral $B_{10}C_2H_{12}$, which are isoelectronic with $B_{12}H_{12}^{-2}$, and which form a very large derivative chemistry. Isopropenyl carborane, prepared by Bobinski, Fein, and Mayes, was apparently first recognized as related to icosahedral (*18*) $B_{12}H_{12}^{-2}$ by Mangold and Hillman (*30*). But the first structure proof was made by crystallographic methods (*31*) on $B_{10}C_2Cl_{12}$, and also later on a number of other derivatives as part of studies aimed at (i) elucidating (*32*) the sequential order of electrophilic and nucleophilic substitution and (ii) the assignment of the B^{11} nuclear magnetic resonance spectrum. Also in 1963 the preparation and reactions of $B_{10}C_2H_{12}$ were described by Zakharkin and co-workers (*33*), who established sequential substitution (*34*) with the additional help of the earlier predictions (*27*) of molecular orbital theory and the results of the $B_{10}H_2Cl_8C_2H_2$ structure study (*35*). After the extensive studies of substitution chemistry on $B_{10}C_2H_{12}$, the substitution chemistry of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ has yielded a large number of new compounds (*36*). The preparation by Williams and Gerhart (*37*) of $B_6H_6C_2(CH_3)_2$ and by Hawthorne and co-workers of *C,C′*-dimethyl derivatives of $B_6C_2H_8$, $B_7C_2H_7$, and $B_8C_2H_{10}$ (two isomers) (*38*), and of $B_9C_2H_{11}$ (*39*) complete the new single polyhedra of the type $C_2B_nH_n$ for $3 < n < 10$.

This article is concerned with the probable mechanisms of rearrange-

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ments which give isomers of these carboranes and their corresponding borane ions $B_mH_m^{-2}$. I wish to show how the idea arose in connection with the studies of the icosahedral and cube-octahedral B_{12} structures and of the $Cu_2B_{10}H_{10}$ structure, then to indicate results of predictions where known, and finally to show the probable consequences of general application of the idea to polyhedral molecules and their fragments.

Mechanism and Predictions for $C_2B_{10}H_{12}$ and $B_{10}H_{10}^{-2}$

In a study (*40*) of the valence structures of the higher borides I had juxtaposed the cube-octahedral B_{12} unit of ZrB_{12} (*41*) with the icosahedral structure (Fig. 2), and had indicated how little atomic motion is required to transform the square face of the former to the diamond-shaped pair of triangles of the latter. Later, I realized (*42*) that the square face of the cube-octahedron could collapse to a diamond at the unmarked corners of Fig. 2*B*, and hence produce an isomerization of the icosahedron which would move two adjacent atoms or substituents into nonadjacent positions. The realization (*43*) that consecutive application of this mechanism would not move adjacent atoms into completely opposite positions, because a center of symmetry is preserved if the transformation is somewhat idealized, then led to a clear statement that o-$C_2B_{10}H_{12}$ (C,C' adjacent) would produce only one isomer, m-$C_2B_{10}H_{12}$, but not p-$C_2B_{10}H_{12}$ (C,C' opposite). Later this meta isomer was reported (*44*) as a result of heating of o-$C_2B_{10}H_{12}$ to 465° to 500°C, but the p-$C_2B_{10}H_{12}$ isomer can only be obtained (*45*) in small (6 to 7 percent) yields at 615°C as the sample decomposes.

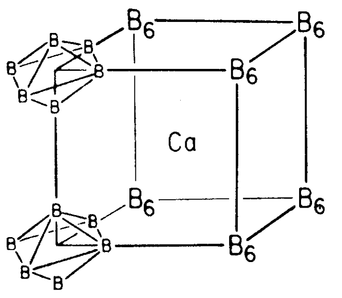


Fig. 1. Structure of CaB_6.

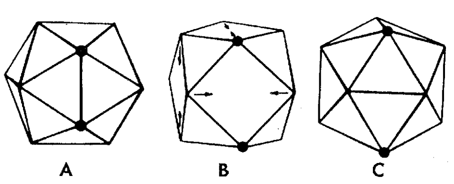


Fig. 2. The small distortions of the B_{12} cube-octahedron which are required to convert it to the icosahedron are shown by the small arrows.

One of the several ambiguities (*46*) leading to nearly correct crystal structures for $Cu_2B_{10}H_{10}$ was the orientation of the B_{10} polyhedron, which has two oppositely situated boron atoms coordinated to four other boron atoms, and eight boron atoms each coordinated to five other boron atoms (Fig. 3). It was this ambiguity which led me to predict the rearrangement shown in Fig. 3, where six boron atoms move about 0.4 angstroms, while the remaining four boron atoms move very little. The initiation of this rearrangement by movement, for example, of atom *J* towards atom *A* would convert the diamond *ACJH* into a square in the transition state, which could then transform by further expansion of the *HC* contact and further contraction of *AJ* to the new diamond shape *ACJH*. This rearrangement was later discovered (*47*), and this proposed mechanism was tested in a number of cases; for example, in $B_{10}H_8[N(CH_3)_3]_2$ the *BC* disubstituted molecule yields only the *AD* product at 220°C.

In the following sections this mechanism will be called the dsd (diamond-square-diamond) rearrangement or mechanism. I should now like to elaborate the consequences which follow from the assumption that this mechanism is a general property of polyhedral boranes, ions, and carboranes, and of other molecules and ions similar to boron hydrides.

Polyhedral Species

A_5X_5($B_3C_2H_5$ and hypothetical $B_5H_5^{-2}$). Spectroscopic evidence, especially nuclear magnetic resonance spectra, indicate that both carbon-hydrogen linkages are equivalent, and that all three boron-hydrogen linkages are equivalent in $B_3C_2H_5$. Hence a trigonal bipyramidal structure of symmetry D_{3h} was indicated (*24*) as most probable (Fig. 4*C*). Probably this conclusion is correct, but it is remarkable that the carbon atoms are nonadjacent in view of the preparation from acetylene, and that only one isomer of $B_3C_2H_5$ is known (*48*).

The molecular-orbital study (*27*) clearly favors this isomer among the three possible isomers based upon the trigonal bipyramid. Moreover, the small nuclear motion required to produce the dsd rearrangement (Fig. 4) probably makes interconversion of these isomers readily accessible. Although the C_{4v} structure of $B_5H_5^{-2}$ is unstable (*22*) with respect to distortion to the D_{3h} structure, the lower symmetry required when two B^- are replaced by two carbon atoms may open the possibility of rapid dynamical interconversion of structures shown in Fig. 4, *A* and *C*, in a structure in which the two CH groups are never adjacent. The same transformation might exist in a predicted structure of C_{4v} symmetry expected (*22*) for B_5Cl_5, which has not yet been discovered.

A_6X_6($B_4C_2H_6$ and $B_6H_6^{-2}$). Both isomers, *cis* and *trans*, are known for $B_4C_2H_6$ which is isoelectronic with predicted and now-known octahedral $B_6H_6^{-2}$. The probable stability of polyhedra having an even number of vertices, as compared with those having an odd number, raises the question as

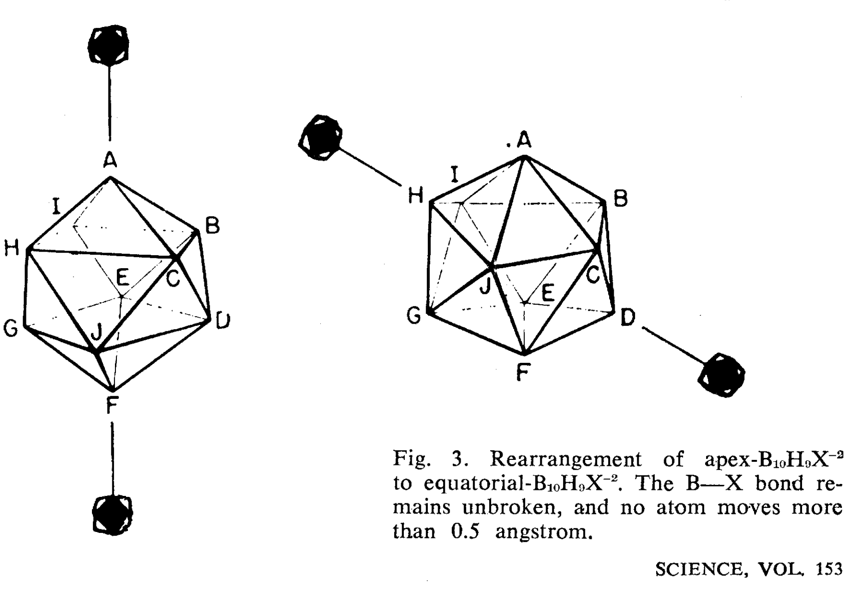


Fig. 3. Rearrangement of apex-$B_{10}H_9X^{-2}$ to equatorial-$B_{10}H_9X^{-2}$. The B—X bond remains unbroken, and no atom moves more than 0.5 angstrom.

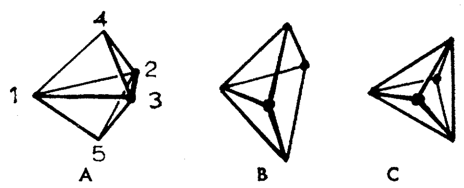


Fig. 4. The dsd rearrangement in $B_5H_5^{-2}$ and $C_2B_3H_5$.

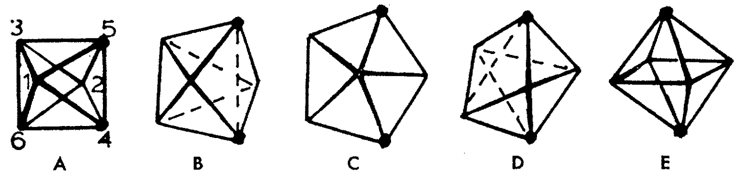


Fig. 5. The pentagonal pyramidal intermediate is shown at *C* for the B_6 dsd rearrangement.

Fig. 6. Trigonal prism intermediate shown at *B*.

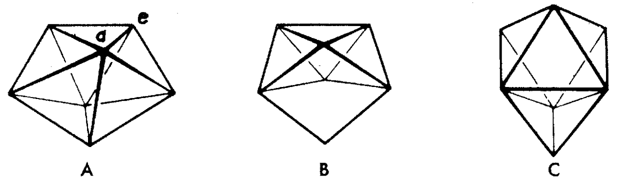


Fig. 7. The intermediate *C*, of C_{3v} symmetry in $B_7H_7^{-2}$, can then go to a different C_{5v} orientation. The transformation could also proceed through the relatively open NbF_7^{-2} type of geometry (C_{2v}), which has two adjacent square and six triangular faces.

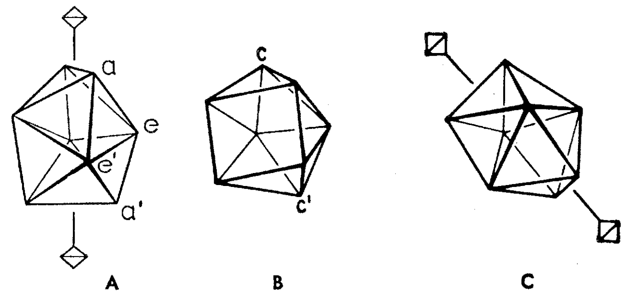
to whether an A_6 polyhedron rearranges as does an A_7 polyhedron where one apex is a vacancy. Probably, this mechanism is important when a generalized base catalyzes the rearrangement, but, unless there really is an atom to occupy the extra position, the intermediates generally have less bonding than those in the dsd rearrangements. Now, for the octahedron, the single dsd rearrangement (Fig. 5) seems more probable than the cooperative-twist dsd rearrangement; perhaps it has a lower energy, but it probably produces fewer problems in internal angular momentum than does the cooperative mechanism (Fig. 6). However, the clearest differentiation of these two dsd mechanisms is discussed below in the case of icosahedral $B_{10}C_2H_{12}$.

A_7X_7($B_5C_2H_7$ and hypothetical $B_7H_7^{-2}$). Complete scrambling of all positions occurs upon successive applications of the dsd mechanism shown in Fig. 7. The molecular-orbital prediction (*27*) gave slightly lower energy to the isomer in which carbon atoms are nonadjacent and in the equatorial positions (*e*), as was later proved (*29*). Here, as in $B_3C_2H_5$, only one isomer is known, again for an odd number of vertices. An *aa* (apical-apical) disubstituted species can go only to *ee*, but more interesting from the viewpoint that acetylene is a starting material for the carborane is that *ee* (adjacent) goes only to *ae* (adjacent) and only then to nonadjacent positions. The geometry of the intermediate could be between one extreme, which has only triangular faces (Fig. 7*C*), and a relatively open NbF_7^{-2} type of structure (*49*), which has two square faces sharing an edge and six triangular faces in a polyhedron of symmetry near C_{2v}.

A_8X_8($B_6C_2H_8$ and B_8Cl_8). A low-lying electronic single molecular orbital is vacant (*50*) in B_8H_8 of D_{2d} symmetry, and hence both B_8H_8 and $B_8H_8^{-2}$ are consistent with filled molecular orbitals. Neither is known, but B_8Cl_8 is known (*21*) and so is $B_6C_2H_8$ (*38*). The dsd rearrangement is particularly facile when an ee′ bond is partially opened (Fig. 8). Perhaps some seven vertex systems may tend to add a vacancy and then prefer this intermediate (Fig. 8*B*) to that shown in Fig. 7*C*. Now in $B_6H_6C_2(CH_3)_2$ only two boron-11 nuclear magnetic resonance peaks have been observed, but at least three different types of boron atoms are present for all possible choices of positions for two carbon atoms in the polyhedron of Fig. 8*A*. Williams and Gerhart (*37*), probably correctly, chose positions *a* and *a′* as carbon positions in the most stable isomer, and hence require an accidental coincidence of two types of boron-11 resonances. On the other hand Tebbe, Garrett, Young, and Hawthorne (*38*) point out that the square antiprism structure is consistent with the boron-11 nuclear magnetic resonance spectrum, but also recognize the possibility of accidental coincidence in the structure proposed by Williams and Gerhart. I now offer an interpretation which differs from both of these, and suggest that the structure in which carbon atoms are at *c* and *c′* in Fig. 8*B* is correct, or (perhaps preferably) that a rapid dynamic interchange toward structures in Fig. 8, *A* and *C*, occurs through the structure in Fig. 8*B*. This suggestion avoids the accidental coincidence required above, and also avoids the relatively open square antiprism structure.

A_9X_9($B_7C_2H_9$ and hypothetical $B_9H_9^{-2}$). The trigonal triprism structure for $B_7C_2H_9$ in which carbon atoms are at two apical positions of Fig. 9*A* has been assigned from the boron-11 nuclear magnetic resonance spectrum, which shows equivalent carbon-hydrogen (CH) units and boron atoms in the ratios 1:2:4. The proposed mechanism of dsd rearrangement places one boron atom just short of the position shown in Fig. 9*B* as coordinated to six other boron atoms. With the terminal hydrogen atom this is a seven-coordinated boron atom which is unusual, but seven coordination of various geometries occurs in $B_{20}H_{16}$ (*51*), $B_{18}H_{22}$ (*52*), and isomeric $B_{18}H_{22}$ (*53*). The rearrangement shown in Fig. 9 scrambles all positions after successive steps.

$A_{10}X_{10}$($B_8C_2H_{10}$ and $B_{10}H_{10}^{-2}$). Since the original prediction (*42*), this rearrangement has been studied in both the $B_8C_2H_{10}$ molecule (*38*) and the disubstituted $B_{10}H_{10}^{-2}$ ion (*47*). In $B_8H_8C_2(CH_3)_2$, two isomers are known, the more stable of which shows that all boron-11 resonances are equal and hence that both carbon atoms are in the apex (Fig. 3) positions as expected from the extra negative charge (*54*) on these apices in $B_{10}H_{10}^{-2}$. The other isomer may have one apical carbon and one equatorial carbon not adjacent to the apical carbon, but an x-ray dif-



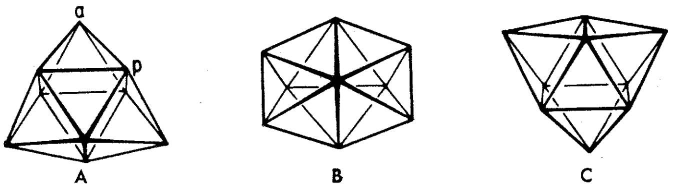


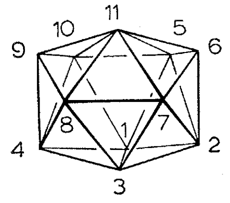
Fig. 8 (left). The intermediate *B* has C_{2v} symmetry in B_8Cl_8.

Fig. 9 (right). The intermediate *B* has C_{2v} symmetry in $B_9H_9^{-2}$.

fraction study is needed to reinvestigate this assignment, which is based partly on the nuclear magnetic resonance spectra and partly on the assumption that the carbon atoms are nonadjacent.

The probability that the isomerization of $B_{10}H_{10}^{-2}$ is a high-temperature process was pointed out some time ago (*55*), although low-temperature, equivalent rearrangements by a different mechanism (OH^- canalyzed) are known in $[B_{10}H_9—B_{10}H_8OH]^{-4}$ isomers (*56*), which were originally thought to be $B_{10}H_9OH^{-2}$ isomers (*42*). A recent detailed study (*47*) of these rearrangements has shown an activation energy of 37 kcal/mole for the rearrangement of $B_{10}H_8[N(CH_3)_3]_2$ at 220°C from positions *BC* to *AD*. Other isomerizations require temperatures about 100°C higher in the 300° to 350°C range. It does appear that the mechanism (*42*) has been carefully tested in these studies (Fig. 3).

$A_{11}X_{11}$($B_9C_2H_{11}$ and hypothetical $B_{11}H_{11}^{-2}$). Although $B_9C_2H_{11}$ is known (*39*) its structure is not. Two proposals have been made, one (*39*) based upon the 11-particle icosahedral fragment, and the other (*57*) based upon a collapse of the open pentagonal face into triangles by formation of two more close contacts (Fig. 10). Here again an x-ray diffraction study is needed. The clear implication of molecular orbitals (*22*) in $B_{11}H_{11}^{-2}$ of C_{5v} symmetry (regular icosahedral fragment) is that there are four electrons to fill an axially symmetric and a degenerate pair of bonding orbitals formed from five atomic orbitals at the open face, and therefore a distortion is indicated. But it is not clear whether one additional short contact, like that suggested (*22*) for $B_{11}H_{13}^{-2}$, or two will be required. A study of the dsd mechanism, in which contact position 8 to 11 (Fig. 10) is opened to make a square which is then collapsed along positions 7 to 9, shows that successive application of this process does scramble all positions.



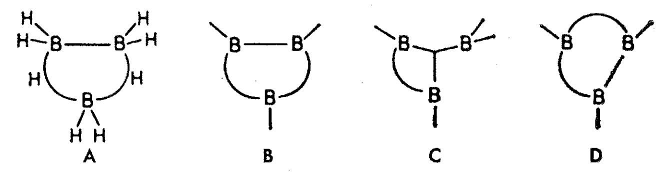


Fig. 10 (left). A C_{2v} structural proposal (*56*) for $B_9C_2H_{11}$. Boron-11 resonances are in ratios 4 : 2 : 2 : 1, so that carbon atoms, if nonadjacent, are possibly at 6,9 or 2,4.

Fig. 11 (right). *A*, Structure of $B_3H_8^-$. *B*, Abbreviated form of *A*. *C*, Presumed intermediate in transformation to *D*, which permutes hydrogen atoms.

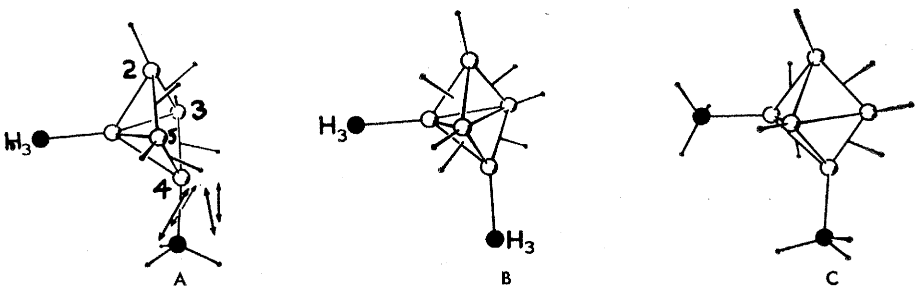


Fig. 12. Rearrangement of 1,2-$(CH_3)_2B_5H_7$ to 2,3-$(CH_3)_2B_5H_7$. The square base *2,3,4,5* contracts along 35 in preference to 24 in order to avoid close contacts between bridge hydrogens and hydrogens on CH_3-B_4.

$A_{12}X_{12}$($B_{10}C_2H_{12}$ and $B_{12}H_{12}^{-2}$). The isomerization of *o*-$B_{10}C_2H_{12}$ to *m*-$B_{10}C_2H_{12}$ by the dsd mechanism is discussed above (Fig. 2). Here we add the qualifying comment that a pathway of slightly lower activation energy may be found if the full cube-octahedral symmetry is not demanded. Thus a vibrational excitation wave could travel over the molecule, so that all six square faces need not be present at the same instant. Clearly, a different mechanism is required at the higher temperatures (by 115° to 150°C) which produce the small yield, at decomposition, of the *p*-$B_{10}C_2H_{12}$. Certainly the cooperative twist of one B_6 icosahedral cap, relative to the other, will produce all isomers, and therefore can be eliminated for the transformation of ortho to meta form.

Isomerization of disubstituted $B_{12}H_{12}^{-2}$ derivatives is consistent with the dsd mechanism shown in Fig. 2, but the results are not as conclusive as they are in the earlier icosahedral carborane studies. Thus *p*-$B_{10}H_{12}[N(CH_3)_3]_2$ does not produce other products up to 530°C. Also the meta product undergoes slight conversion only to *o*-$B_{10}H_{12}[N(CH_3)_3]_2$ at 400°C, but this reaction is complicated by the competing thermal decomposition of this ortho product (*47*).

There is a further effect to be searched for, however, in this well-tested icosahedral case. The higher nuclear charge of carbon requires more electrons in the vicinity than are needed for boron atoms. Indeed the interatomic distances (*58*) in $B_{10}H_2Cl_8C_2H_2$ of C—C equal to 1.67 Å, B—C (average) equal to 1.71 Å, and B—B (average) equal to 1.79 Å are most easily understood if more electrons are given to C than to B atoms. Hence there may be a small preference in *o*-$B_{10}C_2H_{12}$ for dsd rearrangements which do not open the C—C contact, as compared with those which do. If the C—C con-

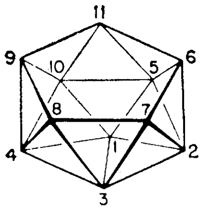


Fig. 13. B_{11} fragment from a regular icosahedron.

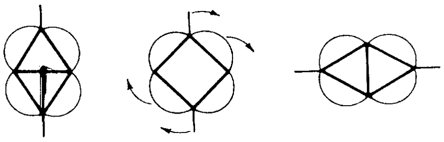


Fig. 14. Proposal for B_4H_{10} rearrangement.

tact is preserved, with slight preference, the substituents on the boron atoms opposite these carbon atoms will tend to remain as near neighbors in rearrangements which, in other parts of the molecule, undergo ortho to meta interconversions, or the reverse. This effect has not yet been reported.

Polyhedral Fragments

Hydrogen atom rearrangements. In the following consideration of the dsd mechanism for rearrangement of framework atoms in the more complex hydrides, it becomes necessary to examine the behavior of hydrogen atoms, which undergo their own kinds of rearrangements. A simple example is the complete permutation of all eight hydrogen atoms indicated (*59*) by the hyperfine structure of the boron-11 nuclear magnetic resonance spectrum of the $B_3H_8^-$ ion (Fig. 11). Here, the boron atoms are magnetically equivalent. In the higher hydrides, ions, and carboranes other kinds of hydrogen-atom rearrangements are also known, some of which probably scramble only bridge hydrogens and extra terminal hydrogens on BH_2 groups, for example, in the B_6H_{10} rearrangement (*60*). It will be assumed here that the hydrogen atoms can follow the boron arrangements in accord with reasonable bond distances and intramolecular steric requirements; and where these requirements appear to impose constraints, explicit effects of hydrogen atom positions will be examined.

B_5H_9 rearrangements [$B_5H_7(CH_3)_2$]. The clearest and most carefully studied rearrangement of a boron polyhedral fragment is that for the dimethyl derivative of pentaborane-9. That there is thermal rearrangement of 1-$CH_3B_5H_8$ to 2-$CH_3B_5H_8$ has been established by nuclear magnetic resonance methods (*61*). Further methylation at the apex and rearrangement (*62*) has yielded a product identified (*63*) by x-ray methods as 2,3-$(CH_3)_2B_5H_7$. A nearly trigonal bipyramidal intermediate formed by contracting the contact from positions 5 to 3 and expanding the contact from position 4 to 2 (Fig. 12) produces fewer repulsions between bridge hydrogen atoms and hydrogen atoms on the methyl group attached to B_2 than does the only other route to this type of intermediate (contract distance 4—2 and expand distance 5—3. I assume that hydrogen atoms move as little as possible, and that only an equatorial-equatorial B • • • B contact of the intermediate can be opened (*64*). The only result of the rearrangement has methyl groups on adjacent basal boron atoms. If the intermediate is $(CH_3)_2B_5H_6^-$ [like $B_5H_8^-$ (*65*)], and if the hydrogen atoms move as little as possible or if they form no BH_2 groups, then the same types of steric interactions lead to the same final product (Fig. 12*C*).

$B_9C_2H_{12}^-$($C_6H_5B_9C_2H_{11}^-$). The steric properties of the extra hydride ion (H^-), over the $B_9C_2H_{11}$ formula, make unlikely complete collapse of the open pentagonal face 6, 7, 8, 9, 11 of the icosahedral fragment (Fig. 13). However, partial collapse is possible, but the extra hydrogen has not yet been identified as a bridge or extra terminal hydrogen. The two known isomers are a result of extraction of boron by ethoxide ion from *o*-$B_{10}C_2H_{12}$ and from *m*-$B_{10}C_2H_{12}$, both B_{10} compounds probably losing the most positive boron atom, which is one of those linked to two carbon atoms in either structure. The *C*-phenyl derivative $B_9C_2H_{11}C_6H_5^-$ from *o*-carborane transforms to the derivative from *m*-carborane at 300°A, and it has therefore been suggested (*66*) that the cube-octahedral mechanism applies also to these B_9C_2 fragments. Probably this dsd rearrangement is indeed a lower-energy pathway than, for example, that of vacancy migrations, but further tests need to be made on other substituted derivatives.

Other hydrides. The dsd mechanism scrambles boron atoms in both B_4H_{10} and B_5H_{11} (Figs. 14 and 15). I therefore propose this mechanism to explain boron-11 tracer studies reported by Schaeffer (*67*). Here, as in the B_5H_9 case, further study of the role of hydrogen atoms is required to show whether rearrangements are occurring in these parent molecules, in those ions produced by loss of H^+, in the ligand adduct itself, or under conditions of intermolecular exchange of hydrogen atoms or BH_3 units. A vacancy migration would most likely only permute the four nonapical atoms of B_5H_{11} around the apical B—H unit, and hence is insufficient to explain the involvement of this apical boron atom. In $B_{10}H_{14}$ all positions are scrambled by the cube-octahedral version of the dsd mechanism, if the two holes, occupied by four hydrogen atoms, are allowed to wander apart. If, however, the four hydrogen atoms must remain in adjacent holes, then all boron atoms except for those (B_1, B_3) opposite the holes are scrambled.

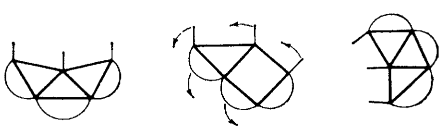


Fig. 15. Proposal for B_5H_{11} rearrangement.

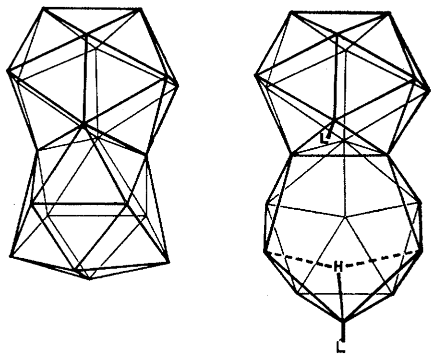


Fig. 16. Rearrangement in the reaction of $B_{20}H_{16}$ with acetonitrile to give $B_{10}H_{16}L_2$, where L is acetonitrile.

When $B_{20}H_{16}$ adds two ligands, L, to form the adduct $B_{20}H_{16}L_2$, others have concluded that the B_{20} unit undergoes no rearrangement. However, an x-ray diffraction study (*68*) indicates that when the ligand is acetonitrile the adduct has the structure shown in Fig. 16. In the process of formation of a closed icosahedron which shares a triangular face with a B_{11} unit there are four regions, all in the lower half of the molecule, where dsd rearrangements take place. The lone bridge hydrogen atom is above the open face, but it is somewhat closer to the boron atom carrying the ligand L than it is to the other boron atoms of this open face.

These rearrangement mechanisms

help to account for the small number of isomers (B_9H_{15}, $B_{18}H_{22}$) among boron hydrides, as compared with hydrocarbons. They may be helpful in certain cases of nuclear resonance equivalences (perhaps $B_9H_{14}^-$). A systematic extension of these principles to rearrangements in molecules and ions having a central atom would surely be profitable, particularly in transition-metal complexes where some limited applications of these ideas already exist.

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