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Contribution from the Department of Chemistry,
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Isomers of $C_2B_3H_5$ and the Diamond–Square–Diamond Rearrangement Mechanism

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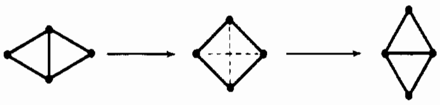
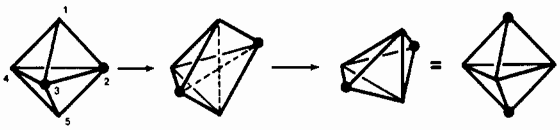
This theoretical study of trigonal-bipyramidal $C_2B_3H_5$ shows that diamond–square–diamond rearrangements are blocked by crossings of filled and vacant molecular orbitals, indicating that these processes face very high activation barriers. Therefore, trigonal-bipyramidal isomers of $C_2B_3H_5$ should be stereochemically rigid, in agreement with available experimental information.

In his 1966 review, Lipscomb[1] described a probable mechanism for the framework reorganization in polyhedral boranes and carboranes with triangular faces. The unifying theme of his proposal is that cage rearrangements occur with the breaking of the bond that forms the edge shared between a pair of adjacent triangular faces and the formation of a new bond perpendicular to the first. The process is called the diamond–square–diamond (DSD) mechanism:



This proposal was a broad generalization of earlier speculation by Lipscomb and Britton,[2] relating cuboctahedral and icosahedral structures for $B_{12}H_{12}^{2-}$, and by Kaczmarczyk, Dobrott, and Lipscomb[3] for the polyhedral isomerization of $B_{10}H_{10}^{2-}$. Hoffmann and Lipscomb[4] extended the proposal to include smaller boron hydrides and carboranes. More recently the idea has been used to describe structural rearrangements in metal clusters.[5]

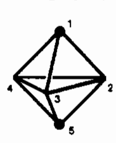
The textbook example for a three-dimensional structure undergoing only a single DSD process is the rearrangement of the trigonal bipyramid through a square pyramid structure to another trigonal bipyramid. Equation 1 shows the process for the rearrangement of the carborane, 2,3-$C_2B_3H_5$ to the 1,5-isomer. The heavy dots represent the carbon heteroatoms. Several authors[6,7] have pointed out that this is a Berry pseudorotation of the kind that is known to take place in rearrangements of trigonal-bipyramidal ML_5 systems such as PCl_5.[8]



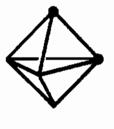
(1)

2,3- 1,5-

There are three possible isomers for the trigonal bipyramidal carborane $C_2B_3H_5$:



1,5-

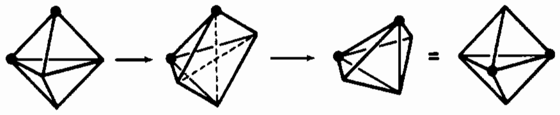


1,2-

2,3-

Empirical valence rules,[9] the rule of topological charge stabilization,[10] and various levels of molecular orbital calculations[11–15] agree that the relative stabilities of the three isomers should be in the order 1,5 > 1,2 > 2,3. Only the 1,5-isomer has been prepared in unsubstituted form.[16] Its structure has been determined by gas-phase electron diffraction.[17]

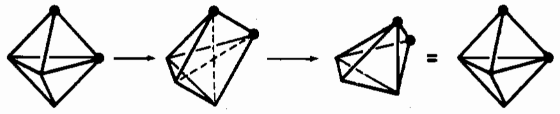
Equation 2 shows the DSD process that carries 1,2-$C_2B_3H_5$ into the 2,3-isomer:



(2)

1,2- 2,3-

A third process, eq 3, is redundant in that it takes the 1,2-isomer into itself:



(3)

1,2- 1,2-

Since eq 3 leads to no new isomer, perhaps it represents "true" pseudorotation for these systems. King has called such a process a degenerate polyhedral isomerization.[7] Equations 1–3 represent the only possible DSD or pseudorotation processes for $C_2B_3H_5$.

Equations 1 and 2 imply that interconversion of all isomers into each other is possible although the transformation of the intermediate energy 1,2-isomer into the lowest energy 1,5-isomer must pass through the highest energy 2,3-form. We wish to point out that both DSD processes (1) and (2) are symmetry forbidden, suggesting that they face activation barriers that are too high to permit thermal rearrangements.[18] Let us begin with eq 1. Both the starting trigonal bipyramid (2,3) and the intermediate square pyramid have C_{2v} symmetry. The 1,5-product has full D_{3h} symmetry. Figure 1 correlates the energies of orbitals between the 2,3- and the 1,5-structures. Only those energy levels near the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) appear in Figure 1. Orbitals are classified according to C_{2v} symmetry, which prevails throughout the process. Orbital energies were calculated by the extended Hückel method.[19] The crossing of b_1 and b_2

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(1) Lipscomb, W. N. *Science (Washington, D.C.)* **1966**, *153*, 373–378.
(2) Lipscomb, W. N.; Britton, D. *J. Chem. Phys.* **1960**, *33*, 275–280.
(3) Kaczmarczyk, A.; Dobrott, R. D.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1962**, *48*, 729–733.
(4) Hoffmann, R.; Lipscomb, W. N. *Inorg. Chem.* **1963**, *2*, 231–232.
(5) Vidal, J. L.; Troup, J. H. *J. Organomet. Chem.* **1982**, *213*, 351–363.
(6) Meutterties, E. L. *Tetrahedron* **1974**, *30*, 1595–1604.
(7) King, R. B. *Inorg. Chim. Acta* **1981**, *49*, 237–240; *Theor. Chim. Acta* **1984**, *64*, 439–452.
(8) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933–938.
(9) Williams, R. D.; Gerhart, F. J. *J. Am. Chem. Soc.* **1965**, *87*, 3513–3515. Williams, R. E. "Carboranes"; Brotherton, R. J., Steinberg, H., Eds.; Pergammon Press: Oxford, 1970; Prog. Boron Chem. Vol. 2, p 37.
(10) Ott, J. J.; Gimarc, B. M., to be submitted for publication.
(11) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489–3493.
(12) Cheung, C.-C. S.; Beaudet, R. A.; Segal, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 4158–4164.
(13) Fitzpatrick, N. J.; Fanning, M. O. *J. Mol. Struct.* **1977**, *40*, 271–277.
(14) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1980**, *19*, 2662–2672.
(15) Graham, G. D.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 2939–2945.
(16) Shapiro, I.; Good, C. D.; Williams, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 3837–3840.
(17) McNeill, E. A.; Gallaher, K. L.; Scholer, F. R.; Bauer, S. H. *Inorg. Chem.* **1973**, *12*, 2108–2111.
(18) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie, CmbH: Weinheim, 1970.
(19) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412. Howell, J.; Rossi, A.; Wallace, D.; Haraki, K.; Hoffmann, R. Program 344, Quantum Chemistry Program Exchange, Indiana University.

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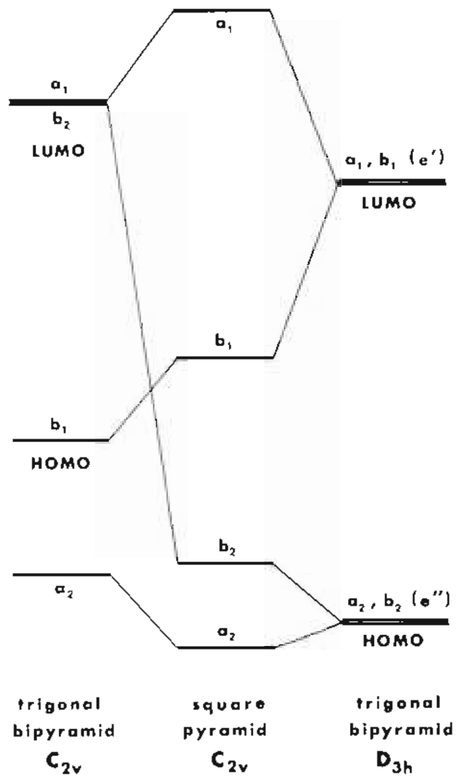


Figure 1. Molecular orbital energy level correlation diagram for the DSD process of eq 1. Only those energy levels are shown that significantly influence the process. The crossing of b_1 (HOMO) and b_2 (LUMO) should block this process.

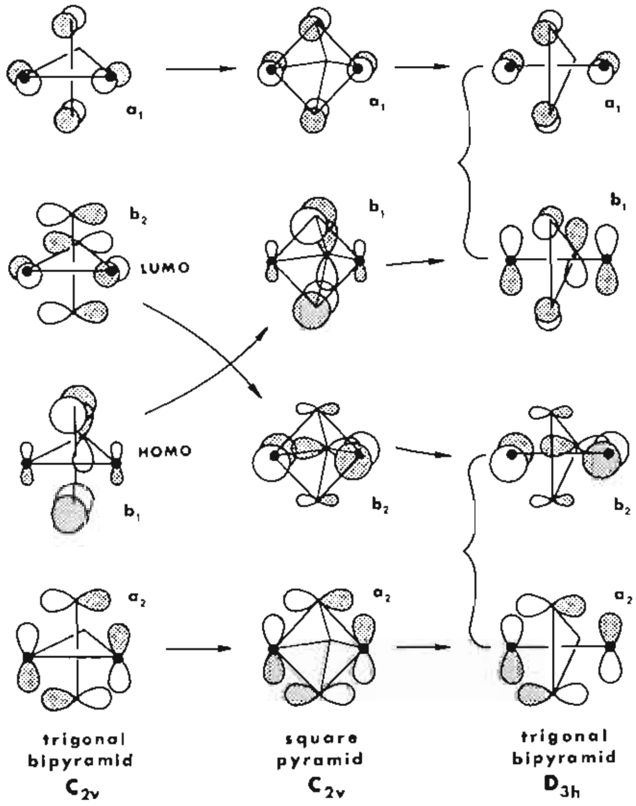


Figure 2. Correlation diagram showing atomic orbital compositions of the molecular orbitals involved in Figure 1.

(HOMO and LUMO) between trigonal bipyramid (C_{2v}) and square pyramid (C_{2v}) indicates a symmetry-forbidden process.

Figure 2 gives the details of this process with correlation of the MOs involved in Figure 1 but showing the AO compositions of individual MOs. Relative energies of the MOs can be rationalized from the phase relationships among the constitutent AOs.[20] For the the 1,5-isomer (full D_{3h} symmetry) Figure 2 presents two sets of degenerate orbitals indicated by the braces: a_2, b_2 (e'') and a_1, b_1 (e'). For the 2,3-isomer a_1 and b_2 are nearly degenerate; they would constitute the e' pair if this structure had D_{3h} symmetry. The a_2, b_1 pair (related to e'' under D_{3h}) are further apart. It is fascinating to see how the nodal properties of these MOs require a switch of orbitals between the e' and e'' sets of the two trigonal bipyramids oriented in different directions.

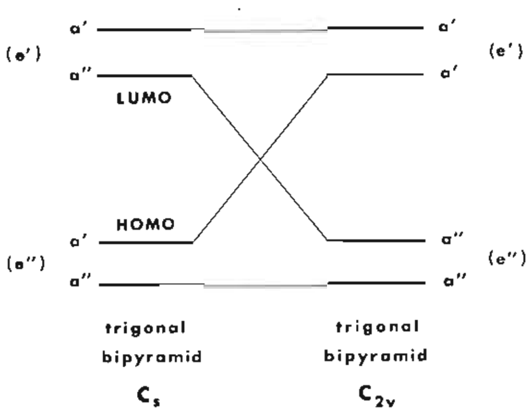
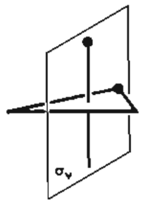


Figure 3. Schematic energy level correaltion diagram for the DSD process of eq 2.

It turns out that the rearrangement of 1,2-$C_2B_3H_5$ into the 2,3-isomer, following the DSD process of eq 2, is also symmetry-forbidden. The symmetry along eq 2 is C_s, lower than that of eq 1, but fortunately we can use the same correlation diagram, Figure 2, with which to analyze this rearrangement. Orbital energies may be somewhat different, but the nodal properties of the orbitals must be the same as those in Figure 2. For the trigonal-bipyramidal C_s structure on the left in eq 2 and Figure 2, assume one carbon is at the top axial vertex and the other is at the rear equatorial vertex with the plane of symmetry σ_v passing through the two heteroatoms and perpendicular to the equatorial plane:



All MOs must be either symmetric (a') or antisymmetric (a'') with respect to σ_v. Reclassifying the MOs of Figure 2 accordingly leads to the modified, schematic energy level correlation diagram in Figure 3. The crossing of HOMO and LUMO (a' and a'') indicates a symmetry-forbidden process.

The DSD mechanism proposed by Lipscomb[1] for isomerization of the trigonal-bipyramidal carborane $C_2B_3H_5$ is prohibited by the principle of conservation of orbital symmetry developed by Woodward and Hoffmann.[18] Therefore, the various isomers of $C_2B_3H_5$ must be stereochemically rigid and unable to rearrange to one another. However, there may be possible isomerization pathways other than the DSD process considered here. Alternative rearrangement mechanisms might involve low-energy "classical structures".[21] Although only the 1,5-isomer is known in unsubstituted form, the dimethyl-substituted derivative of the 1,2-isomer has been prepared.[22] Cage rearrangements among isomers have not been observed in pyrolysis experiments,[23] a result with which our conclusions are consistent.

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(20) Gimarc, B. M. "Molecular Structure and Bonding"; Academic Press: New York, 1979.

(21) Camp, R. N.; Marynick, D. S.; Graham, G. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6781–6783.

(22) Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 1070–1071, 1895–1899.

(23) Grimes, R. N. *J. Organomet. Chem.* **1967**, *8*, 45–51.

Other authors have reported similar theoretical studies for related polyhedral systems. Kleier, McKee, and Lipscomb have found that the DSD mechanism for the rearrangement of tetrahedral B_4H_4 is blocked by a crossing of HOMO and LUMO.[24,25] The tetrahedral–square planar step involved here requires that two bonds be broken simultaneously, a more strenuous situation than is encountered in the trigonal bipyramid–square pyramid step of the $C_2B_3H_5$ rearrangement. Halgren, Pepperberg, and Lipscomb[26] have carried out PRDDO MO calculations to study possible mechanisms for the interconversion of the two isomers of $C_2B_4H_6$. Kleier, Dixon, and Lipscomb[27,28] have also shown on the basis of PRDDO MO calculations that DSD processes are allowed and are of low activation energy in structural rearrangements of $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ for which fluxional behavior has long been known experimentally.[29-31] Lipscomb has suggested that polyhedral rearrangements occurring at high temperatures might involve symmetry crossings of molecular orbitals.[32]

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Registry No. 1,5-$C_2B_3H_5$, 20693-66-7; 1,2-$C_2B_3H_5$, 23777-70-0; 2,3-$C_2B_3H_5$, 30396-61-3.

---

(24) Kleier, D. A.; Bicerano, J.; Lipscomb, W. N. *Inorg. Chem.* **1980**, *19*, 216–218.
(25) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1981**, *20*, 4148–4151.
(26) Halgreen, T. A.; Pepperberg, I. M.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1975**, *97*, 1248–1250.
(27) Kleier, D. A.; Lipscomb, W. N. *Inorg. Chem.* **1979**, *18*, 1312–1318.
(28) Kleier, D. A.; Dixon, D. A.; Lipscomb, W. N. *Inorg. Chem.* **1978**, *17*, 166–167.
(29) Berry, T. E.; Tebbe, F. N.; Hawthorne, M. F. *Tetrahedron Lett.* **1965**, 715–720.
(30) Tolpin, E. I.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1973**, *95*, 2384–2386.
(31) Muetterties, E. L.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 7520–7522.
(32) Lipscomb, W. N. "Boron Chemistry 4", Parry, R. W., Kodama, G., Ed., Pergammon Press: London, 1980; p 1.

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Triply Bridged Diboron Species of the Pyrazabole Type[1]

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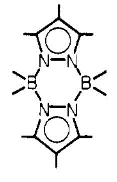
Tri-*B*-organylboroxins, (-BR-O-)$_3$, react with pyrazole, Hpz, to yield pyrazaboles in which the two boron atoms are further bridged by an O-BR-O link, i.e., RB(μ-pz)$_2$(μ-OBRO)BR. The neutral species are structurally related to dibora cations of the type [RB(μ-pz)$_3$BR]$^+$. The preparation of the latter by reaction of either tris(1-pyrazolyl)borate(1-) ions, [RB(pz)$_3$]$^-$, or the pz$^-$ ion with trigonal boranes containing two ready leaving groups, R'BX$_2$, has been studied, and the first unsymmetrical species of the type [RB(μ-pz)$_3$BR']$^+$ is described. In addition, some data on pyrazaboles of the type R_2B(μ-pz)$_2$BR'$_2$ (R = or ≠ R') are reported. They include the preparation and characterization of $(C_6H_5)_2B(\mu\text{-pz})_2B(C_2H_5)_2$, the first known pyrazabole containing different hydrocarbon substituents on the two boron atoms.

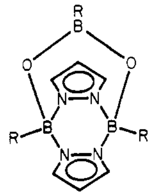
Introduction

The pyrazaboles (=dimeric (1-pyrazolyl)boranes (**1**)) are a chemically remarkably stable class of heterocyles containing four-coordinate boron.[2] Although various boron- and/or carbon-substituted derivatives are known, so far no species containing boron-bonded OH or alkoxy groups have been described. As a matter of fact, the only known pyrazaboles containing B-O bonds are one phenol[3] and two catechol[3,4] derivatives.



1

In our search for B-O derivatives of pyrazaboles, we have accidentally obtained a novel type of pyrazabole, in which the two pyrazabole boron atoms are also bridged by an O-BR-O group. Thus, the species contain not only two four-coordinate borons but an additional three-coordinate boron, as shown in **2**.



2

Dibora monocations of the type [RB(μ-pz)$_3$BR]$^+$, in which the boron atoms are bridged by three pyrazolyl groups, are structurally related to species of type **2**. Only two examples of the former have so far been described in the literature.[5,6] Within the framework of this investigation on diboron species containing the unit B(μ-pz)$_2$B, the specific preparation of [RB(μ-pz)$_3$BR]$^+$ ions has also been studied. Such species were obtained from either pz$^-$ or [RB(pz)$_3$]$^-$ by reaction with trigonal boranes containing two readily leaving groups X, i.e., R'BX$_2$.

This investigation is supplemented by some studies on B- and/or C-substituted pyrazaboles. They include the preparation and characterization of $(C_2H_5)_2B(\mu\text{-pz})_2B(C_6H_5)_2$, the first known pyrazabole containing two different hydrocarbon substituents on the two boron atoms.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY; all compounds gave satisfactory data. Melting points (uncorrected) were determined on a Mel-Temp block. NMR spectra were recorded on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating a downfield shift from the reference (internal Me_4Si for ^1H and ^{13}C; external

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(1) Boron-Nitrogen Compounds. 108. Part 107: Niedenzu, K.; Trofimenko, S. *Inorg. Chem.* **1985**, *24*, 4222. Part 106: Clarke, C. M.; Niedenzu, K.; Niedenzu, P. M.; Trofimenko, S. *Inorg. Chem.* **1985**, *24*, 2648–2651.
(2) "Gmelin Handbuch der Anorganischen Chemie"; Springer-Verlag: West Berlin, 1975; Vol. 23, Supplement Boron Compounds 5, pp 1–8.
(3) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 4948–4952.
(4) Trofimenko, S. *Inorg. Chem.* **1969**, *8*, 1714–1716.
(5) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 5410–5411.
(6) Bradley, D. C.; Hursthouse, M. B.; Newton, J.; Walker, N. P. C. *J. Chem. Soc., Chem. Commun.* **1984**, 188–190.

0020-1669/86/1325-0085$01.50/0 © 1986 American Chemical Society