Table II. Calculated Electron Affinities of $NH_2O^{\bullet}$ and $^{\bullet}NHOH$ and Gas-Phase Acidities of NH_2OH [MP4(SDTQ)-FC/6-311++G**//RHF/6-311++G**][a]

EA, kJ mol^{-1}		ΔH°_{acid},[b] kJ mol^{-1}	
$NH_2O^{\bullet}$	-1.2[c]	$NH_2O\underline{H}$	1629
$^{\bullet}NHOH$	-16.7[d]	$N\underline{H_2}OH$	1669

[a] For individual geometries and energies see Table I. [b] $\Delta H^{\circ}_{acid}(N\underline{H_2}OH)$ = (total energy H^+ + $^{-}NHOH$ + zero point energy correction) − (energy of NH_2OH + zero point energy correction) = (0.0 − 130.79025 + 0.02660) − (−131.44331 + 0.04420) = 0.63326 au = 1669 kJ mol^{-1}. Similarly, $\Delta H^{\circ}_{acid}(NH_2O\underline{H})$ = (0.0 − 130.80685 + 0.02810) − (−131.44331 + 0.04420) = 0.62040 au ≈ 1629 kJ mol^{-1}. [c] $EA(NH_2O^- \rightarrow NH_2O^{\bullet} + e)$ = electronic energy difference (−4.0) + zero point energy difference (2.8) = −1.2 kJ mol^{-1}. The vertical transition energy from NH_2O^- to $NH_2O^{\bullet}$ (at the geometry of the anion) is +41.5 kJ mol^{-1}. [d] $EA(^{-}NHOH \rightarrow {}^{\bullet}NHOH + e)$ = electronic energy difference (−23.6) + zero point energy difference (6.9) = −16.7 kJ mol^{-1}. The vertical transition energy from $^{-}NHOH$ to $^{\bullet}NHOH$ (at the geometry of the anion) is +39.2 kJ mol^{-1}.

unusual transit of H_1 between nitrogen and oxygen; these atoms are splayed to a separation of 2.3 Å at this point. Completion of this transit (out of the displayed grid) reforms **2** or **3** with changed orientation. The reported potential surface of HNO displays an entirely analogous feature: that potential surface is derived from empirical spectroscopic data.[7]

The potential map establishes that NH_2O^- and $^{-}NHOH$ are stable species at normal temperatures. The fact that these ions, particularly $^{-}NHOH$, are difficult to detect experimentally does not then result from the bonding and structural features defined by the potential map. Thus we have calculated the electron affinities of the radicals $^{\bullet}NHOH$ and $NH_2O^{\bullet}$ from the data shown in Table I. In addition, since NH_2O^- and $^{-}NHOH$ are predicted to be powerful bases,[3,5] the two ΔH°_{acid} values of NH_2OH have also been calculated. Calculations were carried out at the MP4(SDTQ)-FC-6-311++G**//HF/6-311++G** level. The electron affinities and ΔH°_{acid} values are summarized in Table II. The data indicate that $^{-}NHOH$ is indeed a powerful base, since the ΔH°_{acid} value of its conjugate acid is 1669 kJ mol^{-1} [cf. $\Delta H^{\circ}_{acid}(NH_3)$ = 1689 kJ mol^{-1} and $\Delta H^{\circ}_{acid}(Me_2NH)$ = 1659 kJ mol^{-1}].[10] However, the electron affinity of $^{\bullet}NHOH$ is appreciably negative (−16.7 kJ mol^{-1}), thus $^{-}NHOH$ should not be directly detectable since it is unstable with respect to its radical. The isomer NH_2O^- is also a strong base: the ΔH°_{acid} value of its conjugate acid is 1629 kJ mol^{-1} [cf. $\Delta H^{\circ}_{acid}(H_2O)$ = 1635 kJ mol^{-1}].[11] In this case, the electron affinity of the radical $NH_2O^{\bullet}$ is very close to zero (−1.2 kJ mol^{-1}); hence it is probable that both $NH_2O^{\bullet}$ and NH_2O^- may be detectable,[12] although the lifetime of NH_2O^- is expected to be short. Hence theory and experiment are in accord for this system.

Acknowledgment. We thank the Australian Research Council for financial support.

Registry No. H^-, 12184-88-2; HNO, 14332-28-6; NH_2O^-, 51375-41-8; $NH_2O^{\bullet}$, 13408-29-2; $^{\bullet}NHOH$, 13940-32-4; NH_2OH, 7803-49-8.

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[9] The potential surface deals with the optimized geometry of HNO with respect to H^-. There is no prior energization of HNO under these conditions and so the surface does not show a channel for elimination of dihydrogen. Instead, H^- moves to add to nitrogen (to ultimately form NH_2O^-). This movement causes disruption of the hydrogen bond and induces rotation of H_2 out of the plane of complex **1** to a dihedral angle schematically represented by the fragment shown in the center of the lower margin of Figure 1.

[10] MacKay, G. L.; Hemsworth, R. S.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1624.

[11] Schulz, P. A.; Mead, R. D.; Jones, P. L.; Lineberger, W. C. *J. Chem. Phys.* **1982**, *77*, 1153.

[12] In this context it is of interest that $NH_2O^{\bullet}$ has been detected experimentally (Davies, P. B.; Dransfeld, P.; Temps, F.; Wagner, H. Gg. *J. Chem. Phys.* **1984**, *81*, 3763). In contrast, $^{\bullet}NHOH$ has not been detected, and indeed it has been suggested that $^{\bullet}NHOH$ may be thermodynamically unstable with respect to $NH_2O^{\bullet}$.[2]

Computational Evidence for a Stable Intermediate in the Rearrangement of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$. A Second Try with a New Twist

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Abstract: The rearrangement mechanism for the conversion of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$ was investigated by ab initio calculations. The reaction proceeds in two steps with a classical benzvalene-like intermediate. The first step, the rate-determining step, is a modified DSD (diamond–square–diamond) step where the symmetry of the transition state is reduced from C_{2v} to C_2 and thus changing the step from orbitally forbidden (in C_{2v} symmetry) to orbitally allowed (in C_2 symmetry). The second step is a concerted DSD step which is also known as a local bond rotation. The activation barrier is calculated to be 44.7 kcal/mol (MP4/6-31G*+ZPC//6-31G*), which is in good agreement with an experimental estimate (42–45 kcal/mol). A third calculated transition state provides a low-energy pathway for the interchange of two sets of equivalent borons in the intermediate.

Introduction

Sixteen years ago a communication with the above title appeared in this journal by Halgren, Pepperberg, and Lipscomb[1] (HPL), who noted that "few reaction pathways in rearrangements of boron compounds are well understood". Although progress has been made,[2-10] this statement is nearly as true today as it was then. The authors (HPL) used a synchronous-transit method[11] to de-

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Table I. Relative Energies (kcal/mol) of Species on the $C_2B_4H_6$ Potential Energy Surface

	sym	HF/ 6-31G* (NIF)[a]	MP2/ 6-31G*	MP4/ 6-31G*	+ZPC
1,2-$C_2B_4H_6$[b]	C_{2v}	0.0 (0)	0.0	0.0	0.0
1,6-$C_2B_4H_6$	D_{4h}	−6.3 (0)	−9.5	−8.6	−8.7
I[c]	C_{2v}	3.9 (0)	32.4	27.0	25.5
TS1	C_2	43.2 (1)	50.9	46.9	44.7
TS2	C_2	26.8 (1)	44.6	39.7	37.6
TS3	C_s	24.1 (1)	40.4	35.3	33.1

[a] The number of imaginary frequencies is given in parentheses. [b] The absolute energies in hartrees of 1,2-$C_2B_4H_6$ at the HF/6-31G*, MP2/6-31G*, and MP4/6-31G* levels are −177.93621, −178.54692, and −178.61010, respectively. [c] Intermediate.

termine the reaction path for rearrangement of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$ and located two transition states and a "sagging sawhorse" intermediate. In a second communication three years later, Lipscomb and co-workers[12] reported that the earlier intermediate was incorrect; the intermediate was actually a benzvalene-like classical intermediate. At the PRDDO level, the intermediate was only 2 kcal/mol above the 1,2-$C_2B_4H_6$ isomer. Despite the interest in carborane rearrangements, a detailed study of this prototypical carborane arrangement mechanism has not been published.[13]

A concerted parallel DSD (diamond–square–diamond) process, known as a local bond rotation,[14] has been proposed in the rearrangement mechanisms of $C_2B_4H_6$ and $C_2B_5H_7$.[13] Several structures, which resemble organic benzvalenes, were evaluated as transition state or intermediate candidates along the arrangement pathway, 1,2-$C_2B_4H_6$ → 1,6-$C_2B_4H_6$. It was determined that the 1,2-$C_2B_4H_6$ isomer could not form a benzvalene-like intermediate with carbons at both bridgehead positions due to an intervening HOMO/LUMO crossing.[4,13] An alternative benzvalene-like intermediate/transition state, the midpoint of a local bond rotation relating 1,2-$C_2B_4H_6$ and 1,6-$C_2B_4H_6$, was considered in which carbon occupied only one bridgehead position.

The present communication reports three transition states and an intermediate along the rearrangement pathway and reveals aspects which may be relevant in rearrangement mechanisms of larger carboranes and other electron-deficient cages. The results are consistent with experiment[15] and provide an interesting insight into two types of mechanisms, the DSD (however, with a "twist") and a local bond rotation. Table I contains relative energies; Figure 1 depicts reactants, transition states, and products in pathways 1, 2, and 3; and Figure 2 gives a minimum energy reaction pathway (MERP) from 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$.

Method

All calculations are carried out with the GAUSSIAN 88 program package.[16] Geometries were optimized at the HF/6-31G* level,[17] and vibrational frequencies were calculated at that level to determine the nature of the stationary point and to make zero-point corrections (0.9 weighting factor). Single-point calculations were made at the full MP4 level of theory with the 6-31G* basis set. A comparison of HF/6-31G* and MP2/6-31G* geometries[18] for 1,2-$C_2B_4H_6$ and 1,6-$C_2B_4H_6$ indicates that electron correlation has little effect on the geometries of these carboranes. When the reactant or product was not clear from an inspection of the imaginary frequency, a small displacement was made in the transition state in a direction indicated by the imaginary mode and the resulting geometry was optimized as a minimum.

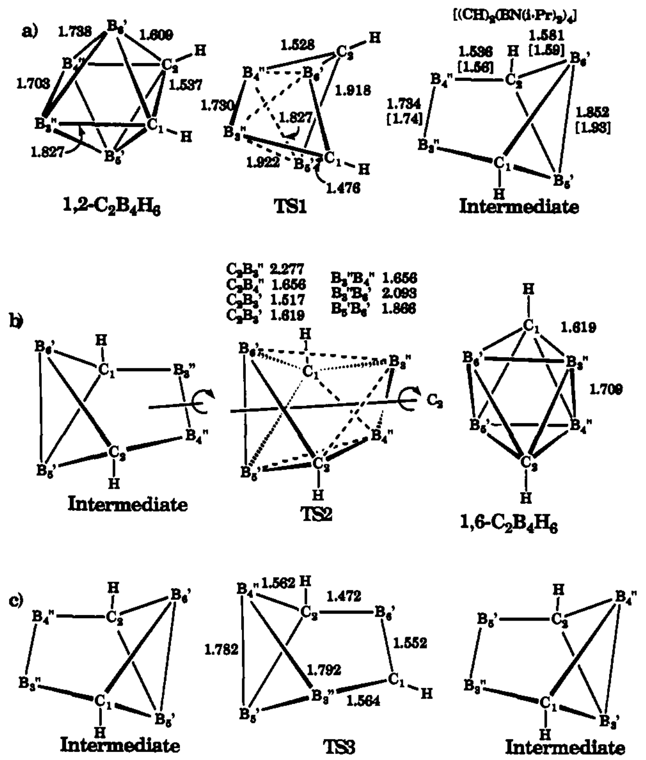

Figure 1. Proposed mechanism for rearrangement of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$. Hydrogens attached to boron atoms are omitted for clarity. Geometric parameters are at the HF/6-31G* level. Values in brackets are from an X-ray determination[23] of the classical intermediate isolated with N(i-Pr)$_2$ groups attached to boron. (a) Step 1 is the formation of a benzvalene-like intermediate by a modified DSD step. With a slight twist, the transition-state symmetry is lowered to C_2 and the step becomes orbitally allowed. (b) Step 2 is the formation of the product 1,6-$C_2B_4H_6$ from the intermediate by a concerted DSD (local bond rotation) step. (c) A transition of C_s symmetry allows the facile interchange of two types of boron atoms in the intermediate.

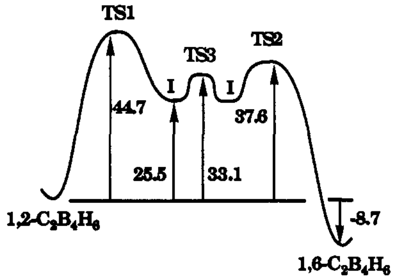

Figure 2. The minimum energy reaction profile (MERP) giving a summary of the barriers encountered in the rearrangement of 1,2-$C_2B_4H_6$. Barrier heights are calculated at the MP4/6-31G*+ZPC//6-31G* level and are given in units of kcal/mol.

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Step 1 (1,2-$C_2B_4H_6$ → I). The first step in the two-step rearrangement is the formation of the intermediate (I), which is the same intermediate identified by Lipscomb and co-workers in their second communication.[12] With respect to 1,2-$C_2B_4H_6$, the activation barrier is 44.7 kcal/mol (Table I), which is within the range estimated[1] (42–45 kcal/mol) from experimental conditions.[15] The step appears to be a DSD rearrangement[19] which was found earlier[13] to be blocked by a HOMO/LUMO crossing. This conclusion was based on a reaction coordinate which maintained C_{2v} symmetry from reactant to the benzvalene-like intermediate. On the reactant side, 1,2-$C_2B_4H_6$, three b_1 orbitals and six b_2 orbitals are occupied, while on the product side, four b_1 orbitals and five b_2 orbitals are occupied. The present determination of the transition state reveals that the first step proceeds in two stages. In the first stage the C_1C_2 bond is elongated while in the second stage the $B_5'B_6'$ bond is contracted (Figure 1a). Near the transition state, the structure assumes C_2 symmetry which mixes orbitals of b_1 and b_2 symmetries, thereby permitting the reaction to proceed in an orbitally allowed fashion. It appears that this symmetry relaxation reduces the barrier of the otherwise orbitally forbidden reaction without adding extra activation energy in the form of steric or electronic repulsion.

Intermediate. The benzvalene-like intermediate is calculated to be 25.5 kcal/mol above the 1,2-$C_2B_4H_6$ isomer and 19.2 kcal/mol below TS1. It can be expected that the intermediate will be difficult to identify and characterize experimentally, except perhaps in a low-temperature matrix. However, substituting an electron-donating group (such as amino substituents) on boron can stabilize the intermediate to the extent that it may become more stable than the nonclassical structure. Thus, substituting NMe_2 in the place of hydrogen on the four borons of *nido*-$C_2B_4H_8$ gives a six-membered ring in the chair conformation.[20,21] Likewise, substituting N(*i*-Pr)$_2$ for hydrogen in *nido*-$C_4B_2H_6$ gives a classical bicyclic organoborane.[22]

The intermediate in the 1,2-$C_2B_4H_6$ → 1,6-$C_2B_4H_6$ rearrangement has been recently isolated and characterized by substituting N(*i*-Pr)$_2$ for hydrogen on the four borons, $(CH)_2$(BN-(*i*-Pr)$_2$)$_4$.[23] The calculated geometry of the benzvalene-like isomer of $C_2B_4H_6$ is in good agreement with the X-ray structure of the N(*i*-Pr)$_2$-substituted form (averaged in C_{2v} symmetry, Figure 1).

Step 2 (I → 1,6-$C_2B_4H_6$). In the second step, the intermediate can undergo a local bond rotation to the 1,6-$C_2B_4H_6$ isomer. The second transition state (TS2) also has C_2 symmetry. In this case, however, there is a smooth variation of parameters from reactant, through the transition state, to product. If one defines a dihedral angle as the angle between B′–B′ and B″–B″ (intermediate = 90° and 1,6-$C_2B_4H_6$ = 0°), then the angle in the transition state is 46.3°, about halfway between the two. At the transition state, the lengths of the two forming B′–B″ bonds are 2.093 Å. The activation barrier is 12.1 kcal/mol with respect to the intermediate and 37.6 kcal/mol with respect to the 1,2-$C_2B_4H_6$ isomer.

I → I. The mechanism proposed so far would predict that the two substituents on boron in the plane of both carbons in 1,2-$C_2B_4H_6$ would always be adjacent in the 1,6-$C_2B_4H_6$ isomer. However, there is a low-energy pathway that will interchange the two sets of boron atoms (B′ and B″, Figure 1c). The boron B_5' can approach B_3'' and B_4'' (breaking interactions with C_1 and B_6') to form a transition state (TS3) which resembles the intermediate but with only one carbon in a bridgehead position. The intermediate (I) is reformed, but with interchanged boron atoms (B′ ↔ B″). Since the degenerate rearrangement occurs with a calculated barrier of 7.6 kcal/mol, compared to a 12.1-kcal/mol barrier to further reaction to 1,6-$C_2B_4H_6$, (Table I), rearrangement of the boron positions should occur during the reaction of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$ (Figure 2).

Conclusion

The calculations presented indicate that the rearrangement of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$ occurs in two steps with the formation of a benzvalene-like species as an intermediate. The first step is rate-determining with a predicted activation barrier of 44.7 kcal/mol. This step, which is orbitally forbidden in C_{2v} symmetry, becomes allowed when the symmetry of the transition state is reduced to C_2.

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Registry No. 1,2-$C_2B_4H_6$, 20693-68-9; 1,6-$C_2B_4H_6$, 20693-67-8; 2,3,5,6-tetraborabicyclo[2.2.1]hexane, 68732-09-2.

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[19] A DSD mechanism requires that a diamond be reformed with opposite vertices connected. While this is true for the rearrangement of 1,2-$C_2B_4H_6$ to the benzvalene-like intermediate (see the four relevant atoms, B_5', B_6', C_1, and C_2 in Figure 1a), the total number of edges is not preserved (12 edges for 1,2-$C_2B_4H_6$ versus 8 edges for the intermediate).

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