Interactions of the $B_3$ cluster with H atoms and $H_2$ molecules

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$Ab$ initio electronic structure calculations on several $\sigma$- and three-center bonded $B_3H$ and $B_3H_2$ structures that correlate with the ground and first excited states of $B_3$ (plus $H$ or $H_2$) have been carried out using correlation-consistent polarized valence double-zeta basis sets and complete-active-space self-consistent-field treatments of electron correlation. Geometries, electronic energies, and local harmonic vibrational frequencies were determined for two locally stable structures of $B_3H$ and three stable and one metastable structures of $B_3H_2$ as well as for transition states connecting such structures. Reaction energies for several processes and a barrier for the $B_3 + H_2 \rightarrow B_3H_2$ reaction have also been calculated. A picture of the $B_3$ reactivity is given in terms of two coupled potential energy surfaces and their avoided crossings. The relevance of our findings to future experimental work and similarities with the chemistry of boranes and related reactive species are emphasized.

I. INTRODUCTION

In a recently published work, we used $ab$ initio quantum chemistry methods to predict the geometries, energies, and harmonic vibrational frequencies of several low-energy electronic states of the Boron trimer. The lowest two states have equilateral triangle geometries yet possess very different electronic structures. The $\tilde{A}^1$ ground state has an electronic orbital occupancy (neglecting the three $1s$ core orbitals' six electrons) in which three $B-B\sigma$ bonding orbitals (of $a_1$ and $e'$ symmetry) are doubly occupied, a delocalized $B-B-B\pi$ orbital (of $a_2^*$ symmetry) is doubly occupied and a nonbonding orbital of $a_1^*$ symmetry shown in Fig. 1 (a) is singly occupied. This orbital occupancy is denoted $1\sigma^22\sigma^33\sigma^21\pi^21n^1$.

The lowest lying excited state is of $^3A^2$ symmetry and is only 7000 cm$^{-1}$ above the ground state and has an orbital occupancy of $1\sigma^22\sigma^23\sigma^21\pi^11n^2$. In this state, an electron is promoted from the $\tilde{A}^1$ ground state's doubly occupied bonding $\pi$ orbital shown in Fig. 1 (b) to the nonbonding orbital of $a_1^*$ symmetry shown in Fig. 1 (a) to form the $^3A^2$ state. As a result, the $\pi$ orbital is half filled in the excited state and the nonbonding $a_1^*$ orbital is doubly occupied.

Because of the different orbital occupancy of these two low-energy states of $B_3$, one expects these two states to undergo quite different reactions; the ground state is a $\sigma$ radical, and the excited state is a $\pi$ radical. The study whose results are described here was undertaken to examine differences in reactivity for these two states of $B_3$ reacting with hydrogen atoms and the simple prototypical $\sigma$ bond of the $H_2$ molecule. In carrying out this study, we were also interested in searching for stable $B_3H$ and $B_3H_2$ geometries and transition states connecting these stable structures as well as in determining vibrational frequencies of such species to guide future spectroscopic studies.

II. CHOICE OF ATOMIC ORBITAL BASIS SETS AND ELECTRONIC CONFIGURATIONS

A. Orbital basis set

The basis set for the boron and hydrogen atoms uses Dunning's correlation-consistent polarized valence double zeta (CC-pVDZ) [9s4p1d/3s2p1d] and [4s1p/2s1p] bases, respectively. The adequacy of the boron basis has been tested as detailed in our previous study of numerous electronic states of the boron trimer.

B. Choice of electronic configurations

In forming a set of electronic configurations, one specifies a set of core orbitals that are doubly occupied in all configuration state functions (CSFs) as well as a set of valence orbitals among which the specified valence electrons are distributed. If the valence electrons are distributed in all possible ways, consistent with overall spin and spatial symmetry of the state of interest, one forms the set of complete active space (CAS) CSFs. This process is especially useful if sever-
al different rearrangements of the molecular framework are to be studied as in the present study where two states of B, two stable B,H structures and transition states connecting them, and several stable and transition-state B3H2 structures are under study.

Because of our interest in several structures, the choice of active valence orbitals for use in constructing our CSFs was guided by the following requirements:

(a) The CSF space must be flexible enough to properly describe at least the nondynamical correlation effects on the two lowest states (i.e., the above \( \sigma \) and \( \pi \) radical states) of the boron trimer because it is to these states that the states of B,H and B,H2 studied here correlate at large interfragment distances.

(b) The CAS wave function should be capable of dissociating properly into the boron trimer and either one or two hydrogen atoms or a hydrogen molecule, depending on the chemical process being studied.

These conditions force one to include the three B-B \( \sigma \) bonding orbitals [labeled \( 3a_1, 4a_1, \) and \( 2b_2 \) in \( C_{2v} \) symmetry appropriate to the most stable B,H isomer identified here—see Fig. 2(a)], the delocalized \( 1\pi \) orbital (labeled \( 1b_1 \)), the nonbonding \( n \) orbital (labeled \( 5a_1 \)), the \( 6a_1 \) and \( 3b_1 \) orbitals for correlation as well as the one or two \( 1s \) orbitals of the one or two H atoms. As in our previous study, the \( 1s \) core \( 1a_1, 7a_1, \) and \( 1b_2 \) orbitals of the boron trimer are doubly occupied in all CSFs. For B3H there are eleven active electrons and nine active orbitals, which give rise to 6048 configurations of doublet spin symmetry.

III. RESULTS

A. Resulting qualitative molecular orbital structures

For the \( C_{2v} \) B3H global minimum structure shown in Fig. 2(a), B–H bonding arises from the interaction of the \( 1n \) orbital in B3 with the \( 1s \) orbital of the H atom and leads to a \( \sigma \) bond–antibond molecular orbital pair. For the higher-energy local minimum structure shown in Fig. 2(b), three-center B–H bonding arises from the interaction of the \( 1n \) and \( \pi \) orbitals of B3 with the H atom's \( 1s \) orbital and produces a bonding, nonbonding, antibonding orbital trio.

B. B3H stable geometries

We found two low-energy minima on the singlet B3H potential energy hypersurfaces. The first, shown in Fig. 2(a), involves a single \( \sigma \) bond between the H atom and a B atom; it can be viewed as arising from simple radical coupling between the \( \sigma \)-radical \( \bar{A} \) state of B3 and an H atom. The geometrical parameters and local harmonic vibrational frequencies of this \( \bar{A} \) symmetry lowest-energy structure are also shown in Fig. 2(a). The dipole moment of this structure is 0.95 D, with the positive end of the dipole directed toward the H atom. The B–H bond strength of this species [i.e., the electronic \( D_e \) to form \( \bar{A} \); B3, and H(\( \bar{2}S \))] is 87 kcal/mol. This bond strength can be compared with the recent accurate calculations\(^4\) of the dissociation energy for diatomic RH (81.5 kcal/mol) Throughout this paper, the energy differences that are reported refer to electronic energies; only when explicitly stated are zero-point corrections included.

The second low-energy structure is of \( \bar{A} \) symmetry in the \( C_2 \) point group and has the geometry and vibrational frequencies detailed in Fig. 2(b). It has a three-center bridge bond involving two B atoms and the H atom, and is 19 kcal/mol less stable than the first structure discussed above. The dipole moment of this structure is 1.42 D, with the H atom again positive. This data suggests that the bridge-bonded H atom is more acidic than the terminally bonded H atom, which is a well known feature in borane chemistry.\(^5\)\(^6\) The dissociation of the bridge-bonded structure to \( B_3 + H \) is
endothermic with $\Delta E = 69$ kcal/mol when ground-state $B_3$ is formed; it is endothermic by 89 kcal/mol if dissociation to the $2^3A_2^+ \pi$ state of $B_3$ is considered. It should be mentioned that the bridge-bonded and terminally bonded structures both lie on the ground electronic state surface of the $B_3H$ species, and both correlate to ground-state $B_3 + H$.

The bond lengths for the above low-energy structures are comparable with the terminal (1.20 Å) and bridge (1.32 Å) bond lengths found in diborane.7 Also the symmetric stretching frequencies fall near the observed values for several boranes.8,9 Terminal $B-H$ (2350-2630 cm$^{-1}$) and bridge $B-H-B$ (1600-2220 cm$^{-1}$).

C. Interconversions among stable geometries of $B_3H$

Transition states (TSs) connecting the two types of stable geometries described above were also located and characterized by geometries, energies, and local harmonic vibrational frequencies. In Fig. 3(a) the reaction path connecting the three-center $\pi$-bridge-bonded $C_3$ structure to the $\sigma$-bonded $C_{12}$ structure is pictured, and the geometric and other characteristics of the corresponding TS, which is of $C_1$ symmetry, are given. This TS lies only 1145 cm$^{-1}$ (732 cm$^{-1}$ or 2 kcal/mol when zero-point corrected) above the three-center-bonded structure. The interconversion of bridge and terminal hydrogen atoms has been previously studied in several boranes.8,9 In particular Lipscomb' interpreted the boron NMR spectrum of $B_3H_8$ which showed equivalence of all boron atoms by assuming a pseudorotation path that permutes all of the hydrogen atoms with an estimated barrier of 0.8 kcal/mol.

In Fig 3(b), we describe the reaction path connecting pairs of equivalent $\pi$-bonded $C_3$ structures passing through a TS having $C_{3v}$ symmetry. Along this path, which has a barrier of 2263 cm$^{-1}$ (2083 cm$^{-1}$ when zero-point corrected), the $H$ atom moves from one side of the plane formed by the three B atoms to the other, preserving one $\sigma_v$ symmetry plane throughout. Another path, which passes through a TS having $C'_3$ symmetry also connects pairs of equivalent $\pi$-bonded $C_3$ structures yet has a barrier of only 979 cm$^{-1}$ (302 cm$^{-1}$ when zero-point corrected). This path is described in Fig. 3(c).

D. $C_{3v}$ structures for $B_3H$

We examined the possibility that a $C_{3v}$ structure could be geometrically stable, but we found that the lowest-energy electronic state for such structures possesses two negative curvatures (of $E$ symmetry) that lead to spontaneous second order Jahn–Teller distortion. Close to the $B_3 + H$ asymptote there is an avoided crossing (5 kcal/mol energy gap) between the two lowest-lying electronic states. The lower state leads to the above Jahn–Teller unstable state whereas the higher state (i) has a shallow minimum with a $B-B$ internuclear distance of 1.60 Å and a $B-H$ distance of 3.13 Å, (ii) lies only 856 cm$^{-1}$ below the $B_3 + H$ asymptote, and (iii) is unstable when zero-point energies are included. The avoided crossing results from the bonding interaction of the hydrogen atom with the singly occupied $\pi$ orbital of $B_3$ (which
FIG. 4. (a) $\text{B}_3\text{H}_3$ global minimum properties. The state has $^2\text{B}_1$ symmetry in $C_{3v}$. (b) $\text{B}_3\text{H}_3$ local minimum properties. The state has $^2\text{A}_1$ symmetry in $C_{3v}$. (c) $\text{B}_3\text{H}_3$ metastable state properties. The state has $^2\text{A}^*$ symmetry in $C_2$. (d) $\text{B}_3\text{H}_3$ linear-state properties. The state has $^2\Pi_1$ symmetry. (e) Transition state properties for the interconversion of global minimum and the metastable state of $\text{B}_3\text{H}_3$. The transition structure has $^2\text{A}^*$ symmetry in $C_2$. (f) Transition state for the $\text{B}_3 + \text{H}_2$ reaction. The state has $^2\text{A}^*$ symmetry in $C_2$. (g) Product geometry for the $\text{B}_3 + \text{H}_2$ reaction. The state has $^2\text{A}^*$ symmetry in $C_2$; it is not the global $\text{B}_3\text{H}_3$ minimum (this structure must further rearrange to form the global minimum).
correlates with the first excited state of boron trimer) and the corresponding repulsive interaction when the \( \pi \) orbital is doubly occupied (which correlates with the ground state of the trimer). In \( C_{3v} \) both orbital occupations correspond to \( A_1 \) symmetry.

### E. \( \text{B}_3\text{H}_2 \) structures

Four local minima were found for \( \text{B}_3\text{H}_2 \). The lowest-energy structure is depicted in Fig. 4(a), and corresponds to a bent structure having two terminal \( \text{B}--\text{H} \) bonds and a dipole moment of 1.36 D. This structure has \( 2B_1 \) electronic symmetry in the \( C_{3v} \) point group; the unpaired electron occupies an out-of-plane \( \pi \)-type orbital distributed over the three \( \text{B} \) atoms. Its geometry and local harmonic vibrational frequencies are given in Fig. 4(a).

A second locally stable structure is shown in Fig. 4(b), where its geometry and vibrational frequencies are given. It has one terminal \( \text{B}--\text{H} \sigma \) bond and one three-center \( \text{B}--\text{H}--\text{B} \) bridge bond and a dipole moment of 1.17 D. It has \( 2A_1 \) symmetry in the \( C_{3v} \) point group and lies 15 kcal/mol above the lowest energy structure. Its unpaired electron resides in an in-plane orbital localized on the two \( \text{B} \) atoms involved in the bridge bond.

Only 5.8 kcal/mol above the global minimum \( 2B_1 \) state is a linear \( 2B_1 \) state [see Fig. 4(d)]. This degenerate state correlates with the lower-energy \( 2B_2 \) state mentioned above as well as with a state of \( 2A_1 \) symmetry when the molecule is bent. As can be seen from the harmonic vibrational frequencies this state presents Renner–Teller instabilities.

In addition to the two stable structures described above, we found a third local minimum that corresponds to a metastable state [see Fig. 4(c)] when zero-point energies are included. This structure has \( 2A_1 \) symmetry and lies 25 kcal/mol above the lowest energy structure. This metastable state was found by following the lowest in-plane Hessian eigenmode starting at the \( 2B_1 \) global minimum passing through a transition state [see Fig. 4(e)] and finally going down to another local minimum (the metastable state). The electronic barrier height (measured from the local minimum) was found to be 173 cm\(^{-1}\) (when corrected for zero-point corrections). The zero-point corrections become very relevant. The zero-point corrected height relative to \( \text{B}_3+\text{H}_2 \) is only 4.6 kcal/mol so that zero-point effects become very relevant.

### F. \( \text{B}_3 \), \( \text{B}_3\text{H} \), and \( \text{B}_3\text{H}_2 \) energetics

In Fig. 5 the relative electronic energies (without zero-point corrections) of the stable species described above are summarized. One observation which is important to make is that ground-state \( \text{B}_3, \text{H}+\text{H} \) is higher in energy than ground-state \( \text{B}_3+\text{H}_2 \) by ca. 6 kcal/mol. This implies that the reaction of \( \text{B}_3 \) with \( \text{H}_2 \) to produce \( \text{B}_3\text{H}_2 \) can not, in the absence of tunneling and at room temperatures where \( kT<0.59 \) kcal/mol, proceed through the stepwise abstraction of an \( \text{H} \) atom to give \( \text{B}_3\text{H}+\text{H} \) followed by the addition of a second \( \text{H} \) atom to yield \( \text{B}_3\text{H}_2 \). Therefore, the formation of \( \text{B}_3\text{H}_2 \) in its global ground state, which is a very exothermic reaction (\( \Delta E= -78 \) kcal/mol), must occur via a concerted process if at all.

### G. Transition state for the \( \text{B}_3+\text{H}_2 \) reaction

A variety of initial geometries representing possible approaches of the hydrogen molecule to ground state \( \text{B}_3 \) were investigated in order to find barriers to reaction. We found a transition state [see Fig. 4(f)] whose geometry is close to the reactant’s as expected based on the Hammond postulate. In this transition state the hydrogen molecule is only slightly perturbed (0.770–0.775 Å) and the boron trimer has slightly lowered its symmetry (the largest change in bond length being 1.58–1.64 Å). The \( \text{B}_3 \) plane bisects the hydrogen molecule and is a plane of symmetry of the molecule. The unpaired electron is in an in-plane orbital similar to that in the ground state of the trimer. The electronic barrier height relative to \( \text{B}_3+\text{H}_2 \) is only 4.6 kcal/mol so that zero-point effects become very relevant. The zero-point corrected barrier height is 6.8 kcal/mol. We have not considered the basis set superposition error but its effect should be to slightly increase the barrier height.
Moving down from the transition state to products, we observe the breaking of the H–H and one B–B bond while forming two terminal B–H bonds. The formation of B–H bonds is accompanied by the breaking of the $\pi$ type bond in $\text{B}_3$, which is responsible for the relative stability of ring over linear structures in the isolated $\text{B}_3$ fragment. One of the boron atoms involved in the bond-breaking process (atom #3 in Fig. 4(f)] executes a large amplitude motion until it finally reaches the minimum structure depicted in Fig. 4(g)]. Here, the unpaired electron resides mainly in a $\rho$ type orbital on the terminal boron atom directed collinearly with all boron atoms. This minimum lies 27.9 kcal/mol above the global $\text{B}_3\text{H}_2$ ground state. It can be thought of as correlating with one component of the $^3\Pi_u$ state of linear $\text{B}_3$. A low-lying excited state correlating with the other degenerate component of $^3\Pi_u$ is observed at 55.3 kcal/mol relative to the $\text{B}_3\text{H}_2$ global minimum (this estimate uses the CI energy of the first excited state with the orbitals optimized for the ground state), which is also bound with respect to ground-state $\text{B}_3 + \text{H}_2$.

H. Related work

The chemisorption of hydrogen onto metal and semiconductor surfaces has been the subject of a considerable amount of theoretical research using cluster models. In particular, chemisorption onto boron surfaces is the subject of a previous ab initio study. In that work, a six-membered cluster was fixed in the shape of a capped pentagon opposed to global, minima were found.

The hydrogen abstraction reaction $\text{B}_3 + \text{H}_2 \rightarrow \text{B}_2\text{H} + \text{H}$ is found to have an endothermicity of 6 kcal/mol. Assuming that an additional dynamical barrier for this process of at least 1 kcal/mol exists, the direct $\text{B}_3 + \text{H}_2 \rightarrow \text{TS} \rightarrow \text{B}_2\text{H}_2$ addition of a hydrogen molecule is predicted to be the lower energy reaction path for the $\text{B}_3 + \text{H}_2$ system. The barrier for the latter process is 6.8 kcal/mol.

Two stable isomers of $\text{B}_3\text{H}$ were studied. Their interconversion, as detailed in this work, could be used as a simple model for the bridge to terminal hydrogen exchange present in some boranes and related inorganic reactive species. The low barriers to interconversion of equivalent bridge-bonded structures should be reflected in the tunneling splittings observed in vibrationally resolved spectra.

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