The B_3Li molecule's electronic and geometrical structure

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The geometries, electronic energies, dipole moments, and local harmonic vibrational frequencies of the singlet ground and low-energy singlet valence excited states of B_3Li have been investigated using (i) correlation-consistent double-zeta plus polarization basis sets, (ii) small valence-space complete active space multiconfiguration self-consistent field electronic wave functions, and (iii) analytical energy derivative techniques combined with automated potential energy surface "walking" algorithms. The lowest-energy structure of B_3Li is found to have C_{3v} symmetry and to consist of a Li atom that sits above the center of an equilateral B_3 moiety; the dipole moment of this species is 6.7 D and its dissociation energy (not zero point corrected) to ground state B_3+Li is 60 kcal/mol. The B_3H analog of this C_{3v} structure is not a geometrically stable species for reasons that are analyzed here. A second stable structure (with dipole moment of 8.5 D and dissociation energy of 47 kcal/mol) is planar and has the Li atom σ bonded to one of the B atoms in the triangular B_3 group. The B_3H analog of this σ-bonded species is stable and, in fact, is the lowest-energy structure of B_3H. Finally, in contrast to findings for B_3H, no bridge-bonded structure was found to be stable for B_3Li. Both the σ-bonded and C_{3v} structures of B_3Li are shown to possess significant charge–transfer character near their equilibrium geometries, but to dissociate to ground state neutral B_3+Li fragments.

I. INTRODUCTION

In recent works, 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 B_3 (Ref. 1) and of the B_3H and B_3H_2 molecules.[2] These efforts view B_3 as a prototypical small cluster of main-group atoms, which possesses several low-energy electronic states that may display a wide range of chemical reactivity. The H atom and H_2 molecules are viewed as prototypical radical (H) and bound (H_2) reactant species for which the reagent (B_3) reactant (H or H_2) electronegativity difference is small. In the present study, we examine another monovalent reactant Li for which the electronegativity difference is quite large; the effects of electronegativity on the electronic and geometrical stability of the resultant clusters is a main focus of this work. The respective electronegativities of B, H, and Li are 2.0, 2.1, and 1.0.

A. Earlier results on B_3

In our earlier study,[1] the lowest two states of B_3 were found to have equilateral triangle geometries yet to possess very different electronic structures. The $^2A_1'$ ground state has an electronic orbital occupancy (neglecting the three $1s$ core orbitals' six electrons) in which all three of the B–B σ bonding orbitals (of a_1' and e' symmetry) are doubly occupied, a delocalized B–B–B π orbital (of a_2'' symmetry) is doubly occupied and a nonbonding orbital $1n$ of a_1' symmetry [shown in Fig. 1(a)] is singly occupied. The latter orbital occupancy will be denoted $1\sigma^2 2\sigma^2 3\sigma^2\ 1\pi^2 1n^1$. The lowest lying excited state ($\sim$7000 cm^{-1} above the ground state) is of $^2A_2''$ symmetry and has an orbital occupancy of $1\sigma^2 2\sigma^2 3\sigma^2\ 1\pi^1 1n^2$; i.e., an electron is promoted from the bonding 1π orbital shown in Fig. 1(b) to the nonbonding $1n$ orbital to form the $^2A_2''$ state from the $^2A_1'$ ground state. The fact that these B_3 states distribute their unpaired electron in qualitatively different regions of space (one is a σ radical and the other is a π radical) suggests that the reactivity of these states should be quite different.

B. Review of B_3H findings

Studying the interaction of B_3 with a single H atom, we found[2] two low-energy minima on the resultant B_3H potential energy hypersurfaces. The first, shown in Fig. 2(a), involves a single σ bond between the H atom and a B atom; it can be viewed as arising from the σ-radical $^2A_1'$ state of B_3 coupling to a H atom. The geometrical and energy parameters and local harmonic vibrational frequencies of this $^1A_1$ C_{2v} symmetry lowest-energy structure are also shown in Fig. 2(a). The second B_3H structure is of $^1A'$ symmetry in the C_s 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. Transition states (TSs) connecting the two types of stable B_3H structures described above were also located and characterized by geometries, energies, and local harmonic vibrational frequencies.

In the present study, we compare our earlier findings on B_3H to those for B_3Li. The primary focus was to examine the effects of the large electronegativity difference be-

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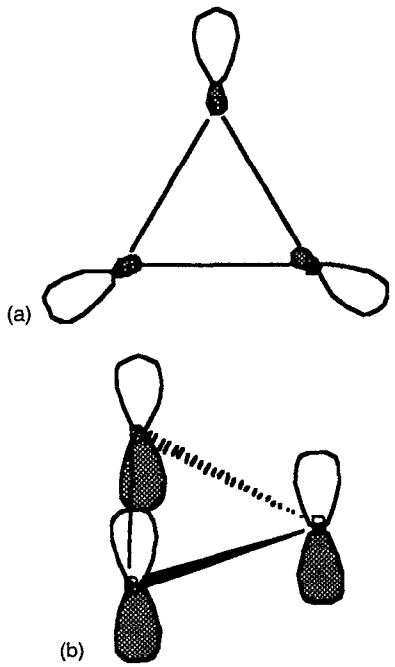

FIG. 1. The two lowest-energy states of B_3 possess singly occupied orbitals of $\sigma_{a_1'}$ (a) and $\pi_{a_1''}$ (b) symmetries, respectively.

tween the monovalent H and Li atoms. Our findings are detailed below in Sec. III.

II. CHOICE OF ATOMIC ORBITAL BASIS SETS AND ELECTRONIC CONFIGURATIONS

For boron, the study was carried out using the [9*s*4*p*1*d*/3*s*2*p*1*d*] correlation-consistent basis atomic orbital basis set of Dunning,[3] chosen because it is capable of treating electron correlation. No corresponding basis set for lithium has, to our knowledge, been developed. Thus the 6–311 G* basis of Krishnan, Binkley, Seeger, and Pople[4] was chosen for lithium because of its ability to reproduce bond lengths and bond energies.[5] The polarization function on Li is due to Binkley and Pople.[6]

Because of the ionic nature of B_3Li, use of additional diffuse *s* and *p* basis functions from Clark *et al.*[7] was considered, because, in some regions of the potential energy surfaces of B_3Li, the charge density has $B_3^-Li^+$ character. However, inclusion of these diffuse functions increased the predicted electron affinity of B_3 by only 5 kcal/mol. Hence, the remainder of this study was carried out without these extra diffuse functions to expedite the calculation, and (small) corrections for resultant errors in state energies that correlate to B_3^- were made.

Our choice of electronic configurations is designed to provide a qualitatively correct treatment of low-lying states, but not to achieve a high-level treatment of dynamical electron correlation. We employed the complete active space multiconfiguration self-consistent field (CAS-MCSCF) method to this end. For C_{3v} geometries, which produced some of the more interesting results reported here, the two lowest-energy totally symmetric (a_1) orbitals and the lowest energy degenerate pair of *e*-type molecular

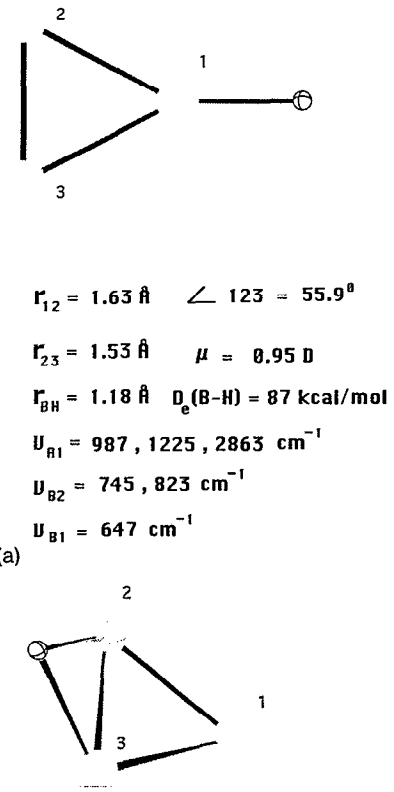

FIG. 2. Two stable structures of B_3H; the σ-bonded structure (a) and the bridge-bonded structure (b).

orbitals were doubly occupied in all configuration state functions (CSFs). These four frozen core orbitals correspond to the three B 1*s* and the Li 1*s* orbitals. The remaining ten electrons were distributed in all possible ways among the next four a_1 orbitals and the next two degenerate pairs of *e* orbitals. Qualitatively, these eight orbitals describe the three B–B σ bonds (a_1 and *e*), the three B-atom nonbonding orbitals (a_1 and *e*) and the bonding and antibonding four-center B_3–Li orbitals (both of a_1 symmetry). This choice of active orbital space resulted in 1176 CSFs of singlet spin multiplicity.

Before deciding on the above choice for the active orbital space, we examined alternatives. In particular, the roles of the three B–B σ^* orbitals (a_1 and *e*) and the two B_3 π^* orbitals (*e*) that do not couple to the Li 2*s* orbital needed to be addressed. Because we had knowledge from

earlier work of our group on the electron affinity (EA) of B_3 and because such energy differences involving different electron numbers pose special difficulties, we decided to compute this EA for various active orbital choices. The primary result of these studies is that the computed EA of B_3 varied by no more than 0.3 eV when the active orbital space (for both B_3 and B_3^-) was increased by the orbitals mentioned above. The EA was found to be largest when the size of the active orbital space was largest. Because we were concerned that truncation of the active orbital space would overestimate the EA, the latter observation was reassuring. The result of numerous such tests lead us to the eight-active-orbital ten-electron valence space introduced above; this choice allowed us to handle, in a computatively feasible manner, the many geometrical "walks" on the ground state surface (which required analytical first and second energy derivatives) needed to locate the stable geometries reported here.

III. SUMMARY OF FINDINGS

A. B_3Li Stable structures

Although we found a stable C_{2v} σ-bonded B_3Li structure analogous to the B_3H structure shown in Fig. 2(a), the analog of the bridge-bonded structure of Fig. 2(b) was found to be not stable. The Li–B bond energy for the stable C_{2v} σ-bonded species is $D_e=47$ kcal/mol, and it has a dipole moment of $\mu=8.50$ D. Its geometry and local harmonic vibrational frequencies are described in Fig. 3(a).

A C_{3v} four-center structure is also predicted to be geometrically stable, and, in fact, to be the global minimum for this species (the analog C_{3v} structure of B_3H was found to be geometrically unstable with respect to displacement of the Li atom in the plane of the B_3 moiety). This B_3Li structure lies 13 kcal/mol below the above σ-bonded species and has a dissociation energy to produce $(X\,^2A_1)$ B_3 + Li of $D_e=60$ kcal/mol. Its geometry and local harmonic vibrational frequencies are described in Fig. 3(b). The dipole moment of this molecule is $\mu=6.7$ D, which corresponds to a fractional charge transfer of $q=0.64\ e^-$ from Li to the center of the B_3 plane. The relatively large electron affinity of B_3 ($\sim$1.5 eV as computed in this work, compared to 0.28 eV for the B atom) is the source of this high degree of charge transfer.

B. Charge–transfer nature of the B_3Li bonding

The B_3Li molecule provides an interesting study in bonding and structure because of the presence of several low-energy electronic states. For C_{3v} geometries, as the Li atom is withdrawn from the center of the B_3 triangle, the dipole moment μ increases as shown in Fig. 4 where the lowest energy singlet state is labeled $^1A_1$. From the dipole moment it is clear that the electronic nature of the $X\,^1A$ B_3Li state changes drastically near $R\cong$4.2–5.2 Å, where the molecule evolves from a charge–transfer complex in which $q\cong0.6$ to one in which one valence electron resides on the Li atom and one remains with the B_3 moiety. Over this range of R values, the dipole moment μ decreases from 12 to 1.5 D.

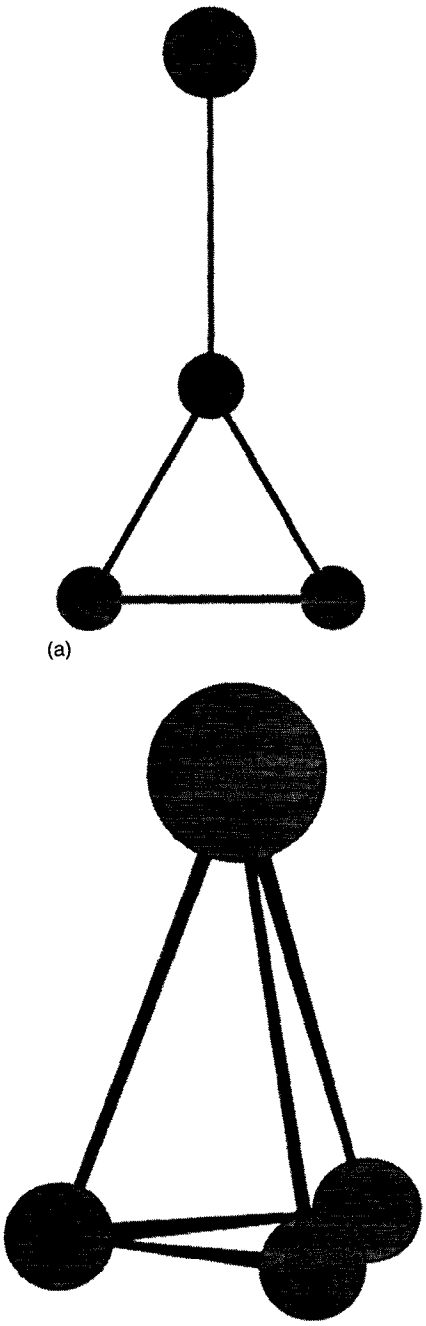

FIG. 3. (a) The C_{2v} σ-bonded structure of B_3Li. The vibrational frequencies (in cm^{-1}) and their symmetries are: $76(b_1)$, $78(b_2)$, $433(a_1)$, $923(a_1)$, $971(b_2)$, $1254(a_1)$. The B–Li bond length is 2.15 Å, the two equal B–B bond lengths are 1.58 Å, and the unique B–B bond length is 1.56 Å. (b) The C_{3v} lowest-energy structure of B_3Li. The vibrational frequencies (in cm^{-1}) and their symmetries are: $237(e)$, $452(a_1)$, $954(e)$, $1251(a_1)$. The B–B bond lengths are 1.57 Å, and the B–Li distance is 2.18 Å.

Dissociation of the C_{3v} structure of B_3Li discussed above produces B_3 in its $X\,^2A_1'$ state and Li (^2S). Dissociation of the C_{2v} σ-bonded B_3Li structure also produces B_3 in its ground state and Li (^2S), so both structures lie on the same potential energy surface. The large dipole moment (8.5 D) of the σ-bonded structure indicates that charge transfer also plays an important role in its bonding.

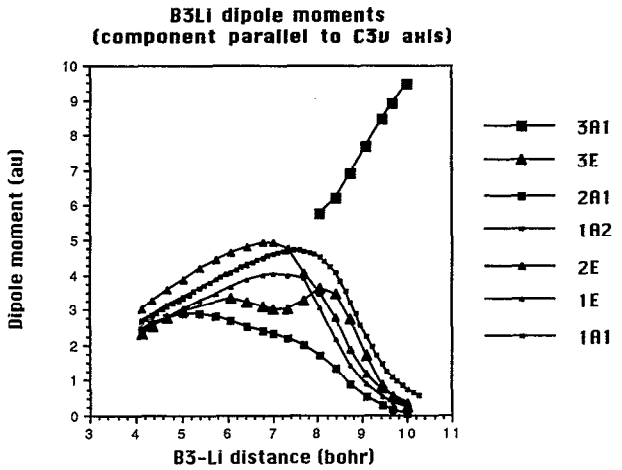

FIG. 4. Dipole moments (1 a.u.=2.54 D) of several low-lying singlet electronic states of C_{3v} B_3Li as a function of the B_3–Li distance (in bohr =0.529 Å units). The state labeled $3A1$ (the third state of A_1 symmetry) dissociates to $B_3^- + Li^+$; the other states all correlate to B_3+Li asymptotically. The states of E symmetry cause the lowest vibrational frequency of e symmetry to be quite small, but do not render the in-plane movement of the Li atom geometrically unstable (see the text).

C. Stability of the C_{3v} structure of B_3Li and instability of C_{3v} B_3H

The appearance of low-energy excited states of ^1E symmetry had a profound role in determining the instability of the C_{3v} structure in B_3H and the stability of the corresponding C_{3v} structure of B_3Li. Second order Jahn–Teller coupling of the $X\,^1A_1$ and low-energy ^1E states of B_3H, induced by distortions of e symmetry (e.g., movement of the H atom parallel to the B_3 plane) caused the $^1A_1$ surface to be geometrically unstable at such C_{3v} geometries. In the present B_3Li case, low-lying ^1E states are again present; the lowest state lies $\sim$80 kcal/mol above the $^1A_1$ ground state at the C_{3v} geometry of Fig. 3(b). However, unlike the B_3H analog, the second order Jahn–Teller couplings between the ^1E and $^1A_1$ states are not strong enough to render the $^1A_1$ state unstable with respect to e-symmetry motion of the Li center. As a result, the C_{3v} geometry is stable for B_3Li, even though it was unstable for B_3H.

IV. SUMMARY

The primary findings reported here are

(1) B_3Li has been found to possess two geometrically stable isomers—one of C_{3v} symmetry and a second σ-bonded structure of C_{2v} symmetry. The two isomers differ in electronic energy by 13 kcal/mol. Both involve charge transfer in their ground state bonding, and thus have very large dipole moments (6.7 and 8.5 D, respectively).

(2) Both isomers dissociate to ground state B_3 (which has an electron affinity of $\sim$1.5 eV) and Li (^2S); the former with D_e=60 kcal/mol, the latter with D_e=47 kcal/mol.

(3) No stable bridge-bonded structure analogous to that of B_3H was found to be stable for B_3Li.

(4) The presence of low-lying excited states of ^1E symmetry does not render the C_{3v} structure of B_3 Li second order Jahn–Teller unstable; for B_3H, the corresponding ^1E states do cause the C_{3v} structure to be geometrically unstable.

(5) The large electronegativity difference between H and Li makes the bonding and structures that arise in B_3Li quite different from those in B_3H.

ACKNOWLEDGMENTS

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