Structure, Bonding, and Stability of Small Boron−Lithium Clusters

Kiet A. Nguyen[†,§] and Koop Lammertsma*[,†,‡]

*Department of Chemistry, University of Alabama at Birmingham, Chem205, UAB Station,
Birmingham, Alabama 35294-1204, and Department of Chemistry, Vrije Universiteit,
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*

Structures and energies for BLi_n ($n = 1-3$) are investigated with various basis sets and with different levels of theory, including single reference- and multireference-based correlated methods up to QCISD(T)/6-311+G-(3df)//MP2(full)/6-311+G(d), MCQDPT2/6-311+G(2df)// CASSCF/6-31G(d), G2, and G2(MP2) theory. BLi ($^3\Pi_g$), BLi_2 ($^2B_2$), and BLi_3 (C_{2v}) are global minima with respective atomization energies of ~26, 55, and 95 kcal/mol. Their structures are not strongly influenced by the size of the basis set nor by the method of electron correlation employed. Energetics for low-lying excited states of BLi and BLi_2 were determined. The dissociation energies obtained with B3LYP/6-31G(d) theory are in excellent agreement with those obtained with the highest levels of theory.

Introduction

Clusters are of considerable interest in research on materials ranging from ceramics to electronics and because of their impact on phenomena such as chemisorption, catalysis, and crystallization. Theory provides an important means to understand the electronic structures and energetics of clusters, and increasingly contributes toward the development of clusters for practical applications.[1−3] Our attention is focused on binary clusters composed of the elements boron and lithium. Lithium boride has been extensively studied as anode (bulk) material in lithium batteries,[4] whereas its smaller clusters[5−10] are of interest as high-energy additives to cryogenic hydrogen. An understanding of the bonding and energetics of these species is fundamental to the design of fuel additives. We are exploring the properties of the smaller clusters, analogous to the lithium clusters of carbon, oxygen, and sulfur.[11] To investigate such systems by theoretical methods, we found a need to investigate the basic systems because of an apparent lack of comprehensive data. In the present study we therefore report computations on BLi, BLi_2, and BLi_3 at different levels of theory aimed at identifying suitable level(s) of theory for studying larger boron−lithium clusters.

Whereas diatomic lithium boride has already been studied extensively,[4−6,10,12,13] few theoretical studies have addressed larger binary boron−lithium systems.[4,9] We include the diatomic for calibration of BLi_2 and BLi_3. The computed stability of BLi was shown to be rather sensitive to the level of theory employed.[12,13] The first ab initio SCF study by Kaufman and Sachs,[5] and more recently by Meden et al.[4] predicted its $^1\Sigma^+$ state to be unbound, whereas Cade and Huo,[6] using a large Slater basis set, found it to be slightly more stable than the separated atoms. Boldyrev et al.[13] studied BLi at the QCISD(T)/6-311+G(2df)//MP2/6-311+G(d) level and found the ground state to be $^3\Pi_g$ with a binding energy D_e, of 27.2 kcal/mol. The energy differences of $^3\Pi_g$ with the $^1\Sigma^+$ and $^3\Sigma^-$ states were estimated at 6.4 and 10.9 kcal/mol, respectively. Knowles and Murrell,[8] using MRCI with a moderately large basis set (B: 10s7p2d/5s5p2d, Li: 10s4p2d/4s4p2d), obtained a similar binding energy of 25.5 kcal/mol for the ground state. Recently, potential energy curves, spectroscopic constants, and radiative lifetimes of several excited states of the singlet, triplet, and quintet spin states were calculated by Sheehy,[10] using internally contracted MRCI with Dunning's quadruple-ζ basis set, and a D_e of 27.7 kcal/mol for the ground state of BLi was obtained.

The theoretical work on BLi_2 has been limited to UHF/6-31G(d) calculations by Meden et al.[4] These authors also examined the electronic structure and stability of BLi_3 and larger BLi_n clusters at SCF/6-31G(d). The most stable BLi_2 structure was predicted to be bent with a B−Li distance of 2.369 Å and a Li−Li distance of 2.510 Å. They reported a planar D_{3h} structure for BLi_3, with a B−Li distance of 1.836 Å. Earlier, using CASSCF with a double-ζ basis set, Saxon[9] showed that the D_{3h} and the T-shaped C_{2v} structures of BLi_3 are essentially isoenergetic. However, the planar D_{3h} form has two small degenerate frequencies at MP2, with imaginary normal modes leading to the C_{2v} isomer.

To shed more light on these small binary clusters and to assist in their gas-phase detection, we examine the structures, energies, and thermal stabilities of BLi_n ($n = 1-3$) using ab initio electronic structure theory. To explore their fragmentation, we consider all possible dissociation channels (reactions 1−8). Enthalpies of reaction for $BLi_n \rightarrow B + Li_n$ reflect the stabilization in the BLi_n clusters due to the boron atom, whereas the thermodynamics for Li and Li_2 elimination is estimated from the reactions $BLi_n \rightarrow BLi_{n-1} + Li$ and $BLi_n \rightarrow BLi_{n-2} + Li_2$, respectively. Other reactions determine atomization and bond dissociation energies (BDEs), which are useful in estimating the stability of clusters of different sizes.

$$BLi_2 \rightarrow B + 2Li \tag{1}$$

$$BLi_2 \rightarrow BLi + Li \tag{2}$$

$$BLi_2 \rightarrow B + Li_2 \tag{3}$$

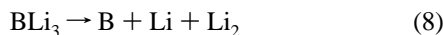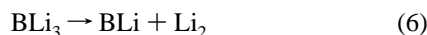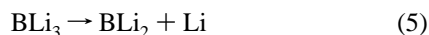$$BLi_3 \rightarrow B + 3Li \tag{4}$$

* Author to whom correspondence should be sent to in The Netherlands.
† Department of Chemistry, University of Alabama at Birmingham.
‡ Department of Chemistry, Vrije Universiteit.
§ Current address: Air Force Research Lab, AFAL/MLPJ, Wright Patterson AFB, OH 45433.

Small Boron−Lithium Clusters

J. Phys. Chem. A, Vol. 102, No. 9, 1998 **1609**

$$BLi_3 \rightarrow BLi_2 + Li \qquad (5)$$

$$BLi_3 \rightarrow BLi + Li_2 \qquad (6)$$

$$BLi_3 \rightarrow B + Li_3 \qquad (7)$$

$$BLi_3 \rightarrow B + Li + Li_2 \qquad (8)$$

Our focus is on the ground-state molecules and their adiabatic dissociation channels, but low-lying excited states of BLi and BLi_2 are also considered. Because some of these boron−lithium systems possess unusual structures, the atoms in molecules (AIM) one-electron density analysis theory[14−16] is used to address their bonding. The effects of basis set and levels of theory on the structures and energies of these small BLi_n clusters ($n = 1-3$) are evaluated. Because our interest extends to larger clusters, we tested the applicability of the more economical density functional theory (DFT) formulation of Kohn and Sham (KS).[17]

Computational Methods

The structures of all BLi_n isomers are optimized at the Hartree−Fock (HF) Self-Consistent Field (SCF) level,[18,19] Møller−Plesset second-order perturbation theory (MP2),[20,21] and KS theory[17] using the 6-31G(*d*),[22] 6-311G(*d*),[23] and 6-311+G-(*d*)[24] basis sets. Additional sets of *d* and *f* functions are used to study the basis set effect further. DFT calculations were carried out using the Becke's three-parameter hybrid functional,[25−27] hereafter referred to as B3LYP. Because BLi_n may have significant configurational mixing and low-lying excited states, requiring a multiconfigurational description, geometries are also evaluated with the Complete Active Space SCF (CASSCF) wave functions.[28]

All structures were verified to be either minima or transition states by evaluation of the force constant matrixes, obtained analytically or from finite differences of the analytically determined gradients. Enthalpies of formation for the single-configurational-based wave functions are reported at G2[29] and G2-(MP2).[30] These methods employ MP2/6-31G(*d*) optimized geometries. G2 energies are obtained from quadratic configuration interaction (QCISD(T))[31] using the 6-311G(*d,p*) basis set with various basis set additivity corrections (diffuse and polarization functions) at the frozen core full fourth order perturbation theory (MP4(SDTQ)) and at the MP2 level, an empirical correction, and a 0.8929 scaled SCF/6-31G(*d*) zero-point vibrational energy (ZPE) correction. The empirical correction of $(-0.19n_\alpha - 4.81n_\beta) \times 10^{-3}$ au is denoted as E(HLC). The G2(MP2) energy expression is simpler. It uses the QCISD(T)/6-311G(*d,p*) energy with basis set additivity corrections at MP2 and the same empirical and ZPE corrections as for G2. Both expressions are shown later. The G2 and G2-(MP2) methods have been reported to give a mean absolute deviation from 125 experimental energies of 1.21 and 1.58 kcal/mol, respectively[29,30]:

$$
\begin{aligned}
E(\text{G2}) = {} & E(\text{QCISD(T)/6-311G}(d,p)) + \\
& E(\text{MP4/6-311+G}(d,p)) - E(\text{MP4/6-311G}(d,p)) + \\
& E(\text{MP4/6-311G}(2df,p)) - E(\text{MP4/6-311G}(d,p)) + \\
& E(\text{MP2/6-311G}(3df,2p)) - E(\text{MP2/6-311G}(2df,p)) - \\
& E(\text{MP2/6-311+G}(d,p)) + E(\text{MP2/6-311G}(d,p)) + \\
& \qquad\qquad E(\text{HLC}) + E(\text{ZPE}) \quad (9)
\end{aligned}
$$

$$
\begin{aligned}
E(\text{G2(MP2)}) = {} & E(\text{QCISD(T)/6-311G}(d,p)) + \\
& E(\text{MP2/6-311+G}(3df,2p)) - E(\text{MP2/6-311G}(d,p) + \\
& \qquad\qquad E(\text{HLC}) + E(\text{ZPE}) \quad (10)
\end{aligned}
$$

Energies for multiconfigurational-based wave functions were obtained by the second-order multiconfigurational quasi-degenerate perturbation theory[32] (MCQDPT2) using CASSCF/6-31G(*d*) structures. All electronic structure calculations were carried out using the GAUSSIAN 94[33] and GAMESS[34] programs.

Results and Discussion

We investigated the $^3\Pi_g$ and $^1\Sigma^+$ states of BLi, the $^2B_2$ and $^2B_1$ states of BLi_2 and the C_{2v} and D_{3h} symmetry forms of BLi_3. As part of this investigation, the $^1\Sigma_g$ state of Li_2 and the $^2B_2$ and $^2A_1$ states of Li_3 are included. Structural parameters, total energies, harmonic vibrational frequencies, and bond critical point data are tabulated for BLi, BLi_2, and BLi_3, and their fragments Li_2 and Li_3 (except for critical point data) in Tables 1−8; the total energies for the atomic boron and lithium are included for convenience (Tables 4 and 6). Computer-generated structures of BLi_3 and Li_3 are displayed in Figure 1. We discuss first the influence of the various theoretical methods on the optimized BLi_n clusters, then some bonding characteristics, and finally their energies.

A. Analysis of Theoretical Methods. The SCF, MP2, QCISD, and B3LYP structures were optimized first with the 6-31G(*d*) basis set and then with the valence triple-ζ series expanded with different types of polarization and diffuse functions to give the following basis sets: 6-311G(*d*), 6-311+G-(*d*), and 6-311+G(2*df*). Analysis of the basis set effect on the QCISD and B3LYP geometries was limited to BLi and BLi_3 isomers. Only the smaller 6-31G(*d*) basis set was used for the CASSCF geometry optimizations.

Basis Set Effect. We start with some general observations. Within each selected theoretical method, using different basis sets, changes in geometrical parameters of all systems are <0.05 Å for bond lengths and <1° for bond angles. The exception is the $^2B_2$ state of Li_3 for which the largest difference in the Li−Li distance is found to be 0.08 Å at MP2 between the 6-31G-(*d*) and 6-311+G(*d*) basis sets; this Li−Li interaction is strongly coupled with a flat Li−Li′-Li bend potential. As we increase from the double to the triple-ζ split valence basis set, all systems show a shortening of bond distances, as expected. However, the effects of additional diffuse and polarization functions on the geometrical parameters are negligible and in some cases nonexistent. Because the basis set effect is small for both the SCF and (single-configurational based) correlated structures, the use of the more economical 6-31G(*d*) basis set seems adequate for geometry optimizations of larger BLi_n clusters. We note that the SCF-based correlated methods give reasonable geometries and energies (vide infra) for open shell systems even in cases with significant spin contamination.[35]

Electron Correlation. Next, we examine the effects of different electron correlation methods on the geometries. With each of the basis sets considered, the BLi bond lengths at MP2 and B3LYP are slightly shorter, whereas those at QCISD and particularly CASSCF are slightly longer than the SCF bond lengths. However, the various correlated methods give similar optimized structures when the same basis set is used. The most pronounced differences are found for BLi_3 (C_{2v}) with differences in BLi bond lengths of −0.04 Å between the SCF and B3LYP methods, of +0.07 Å between the SCF and CISD methods, and of +0.12 Å between the MP2 and QCISD methods (all with

TABLE 1: Structural Parameters and Total and Relative Energies for BLi Isomers[a]

	BLi ($^3\Pi_g$)			BLi ($^1\Sigma^+$)			
level	energy	B–Li	freq.	energy	B–Li	freq.	ΔE
B3LYP/A	32.19043	2.141	539	32.17774	2.416	425	8.0
B3LYP/B	32.19976	2.128	539	32.18573	2.399	431	8.8
B3LYP/C	32.20061	2.131	538	32.18702	2.398	432	8.5
B3LYP/D	32.20124	2.130	537	32.18742	2.397	430	8.7
(U)HF/A	31.97912	2.143	573	31.94303	2.426	450	22.6
(U)HF/B	31.98993	2.131	570	31.95314	2.403	458	23.1
(U)HF/C	31.99077	2.134	568	31.95496	2.401	459	22.5
MP2(full)/A	32.03079	2.138	564	32.01134	2.426	437	12.2
MP2(full)/B	32.07087	2.126	566	32.04997	2.406	443	13.1
MP2(full)/C	32.07222	2.130	562	32.05213	2.404	445	12.6
QCISD/A	32.04416	2.151	548	32.03603	2.459	392	5.1
QCISD/B	32.06064	2.137	549	32.04927	2.425	409	7.1
QCISD/C	32.06189	2.141	548	32.05089	2.420	414	6.9
CASSCF(4,8)/A	32.02309	2.172	533	32.02433	2.474	348	−0.8

[a] Total energies in −au, relative energies (ΔE) for the two isomers in kcal/mol, bond lengths in Å, and frequencies in cm^{-1}. [b] A: 6-31G-(d), B: 6-311G(d), C: 6-311+G(d), and D: 6-311+G(2df).

the 6-31G(d) basis set). Notable differences are also found for Li_2 and Li_3; interestingly their CASSCF/6-31G(d) geometries are more compact than the SCF counterparts. For Li_3 ($^2A_1$), the largest variation in the Li−Li distance of 0.02 Å between B3LYP/6-31G(d) and CASSCF(3,3)/6-31G(d) can be attributed to the flatness of the Li−Li′-Li bend potential. We note that B3LYP predicts a $^2B_2$ ground state for Li_3 and characterizes the $^2A_1$ structure as a saddle point. All other methods identify both structures as minima.

B. Structures and Bonding. The properties of the BLi_n (n = 1−3) global minima are discussed with emphasis on bonding, bond lengths, and vibrational frequencies. We use the 'atoms in molecules' topological one-electron density analysis to evaluate the bonding properties. Details of this method have been described elsewhere.[16,18] We concentrate on the properties of critical points where the gradient of the charge density $\rho(\mathbf{r})$ vanishes. Bond critical points are characterized by a Hessian of $\rho(\mathbf{r})$ with one positive eigenvalue along the bond axis and two negative eigenvalues orthogonal to the bond axis. The Laplacian of the electron density at a critical point $\nabla^2\rho(\mathbf{r})$ determines the region in space wherein the electron charge is concentrated or depleted. The $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ values are summarized in Table 8.

The BLi and BLi_2 Structures. The average bond lengths of BLi ($^3\Pi_g$) using all theoretical levels in Table 1 (except that of the CASSCF structure) is 2.135 Å with a standard deviation (σ) of 0.007 Å. The corresponding average harmonic frequency of 554 cm^{-1} (σ = 14) show BLi to be a well-defined minimum energy structure. The BLi bond critical point is located in close proximity of the Li-nucleus, which reflects the difference in electronegativity between the boron and lithium atoms.

The average bond length of BLi_2 ($^2B_2$) of 2.324 Å (σ = 0.014, Table 2) is longer than that of BLi, and the smallest of its three frequencies of 291 cm^{-1} (σ = 11) is correspondingly smaller. The difference in these BLi bond lengths (8%) is also reflected in the electron densities of their critical points (Table 8). For example, the MP2/6-31G(d) $\rho(\mathbf{r})$ value of 2.07×10^{-2} au for BLi_2 is significantly smaller than the 2.90×10^{-2} au for BLi. Still, the electron density at all BLi bond critical points is small. Their Laplacian values indicate that the electron density distribution around the bond critical points is rather flat, which suggests that BLi_2 is easily deformed from its ideal geometry.

The BLi_3 Structure. All levels of theory predict the C_{2v} structure of BLi_3 to be a minimum, whereas the D_{3h} isomer is also a minimum at the SCF and CASSCF levels (Table 3). Force

field calculations at the MP2, QCISD, and B3LYP correlated levels of theory reveal two small degenerate imaginary frequencies leading to the C_{2v} structure. These results are in agreement with the MP2 and CASSCF data reported earlier by Saxon.[9] Our CASSCF calculations for BLi_3 (D_{3h}) show very little configurational mixing − all the natural orbital occupation numbers (NOONs) for the bonding and antibonding orbitals are close to 2 and 0, respectively (see Figure 2). We next included the effect of dynamic electron correlation and, because gradients at MCQDPT2/6-31G(d) are not available, the BLi_3 potential energy surface was mapped around the CASSCF(6,6) structures to evaluated the $D_{3h} \rightarrow C_{2v}$ relationship. The grid, using 40 points obtained by varying the B−Li distance between 2.0 and 2.4 Å and the Li−B−Li angle between 110° and 130° (see Figure 3), shows that bending the Li−B−Li angle from 120° (D_{3h}) to 130° (with a BLi distance of 2.2 Å) results in an energy gain of 0.15 kcal/mol. Thus, it appears that the shallow minimum obtained at CASSCF(6,6)/6-31G(d) disappears upon including the effects of dynamic electron correlation! Only the C_{2v} form of BLi_3 is a minimum energy structure.

The average B−Li bond lengths (Table 3, except CASSCF) are 2.174 Å (σ = 0.023) and 2.282 Å (σ = 0.047). These distances are slightly longer than that of diatomic BLi and slightly shorter than that of BLi_2. The magnitude of the electron densities at the bond critical points (Table 8) are in line with these bond length variations. The low values of the electron densities at all levels of theory underscore the high degree of structural flexibility for BLi_3 (C_{2v}), which is also in line with the small average value of 109 cm^{-1} (σ = 40) for its smallest harmonic frequency. From these analyses it appears that both MP2 and B3LYP/6-31G(d) provide reasonable geometries for the three global minima of BLi_{1-3}.

C. Energies. In this section we discuss the relative energies, the atomization energies, and the dissociation energies for BLi, BLi_2, and BLi_3. Emphasis is placed on the various theoretical methods and basis sets employed. Relative energies are listed in Table 5, and the atomization energies for BLi and those for the dissociation reactions 1−8 are given in Table 7. Table 7 also lists Li_2 and Li_3 atomization energies and the Li-dissociation energy for Li_3 (listed as reaction 9). For simplicity, we abbreviate QCISD(T)/6-311+G(3df) as QCI and MCQDPT2/6-311+G(2df) as MCQDPT2.

BLi. The energetic preference ΔE of the $^3\Pi_g$ ground state over the $^1\Sigma^+$ state varies strongly with the theoretical method employed, but little with the size of the basis set (see Tables 1 and 5). At our highest levels, ΔE ranges between 6.4 kcal/mol (QCI), also reported by Boldyrev,[13] and 2.3 kcal/mol (G2-(MP2)). This is a surprising result because the G2 method is calibrated largely on diatomics to approximate the QCISD(T)/6-311+G(3df)//MP2/6-31G(d) level.[31] Excluding the G2 empirical correction, ΔE(HLC) gives an energy difference of 5.2 kcal/mol for the two spin states. Because no significant configurational mixing occurs, electron correlation corrections with single reference-based methods, such as MPn and QCISD-(T), are expected to be adequate. Evidently, MCQDPT2 predicts ΔE of 6.1 kcal/mol, a mere 0.3 kcal/mol smaller than QCI. The modest MP2 and particularly UHF give much larger energy differences, whereas B3LYP/6-31G(d) seems to perform rather well with a ΔE of 8.0 kcal/mol. The basis set effect on going from the modest 6-31G(d) to the much larger 6-311+G(2df) is evident for the CASSCF(4,8) and MCQDPT2 methods with respective increases in ΔE of 4.3 and 1.5 kcal/mol.

BLi ($^3\Pi_g$) has a bond dissociation energy D_o of 26.6 kcal/mol at QCI. A nearly identical value of 26.5 kcal/mol is

Small Boron−Lithium Clusters

J. Phys. Chem. A, Vol. 102, No. 9, 1998 **1611**

TABLE 2: Structural Parameters and Total and Relative Energies for BLi$_2$ Isomers[a]

| | BLi$_2$ ($^2B_2$) | | | | | BLi$_2$ ($^2B_1$) | | | | | |
level	energy	$\langle s^2 \rangle$	B−Li	Li−Li	freq. (a_1, b_2, a_1)	energy	$\langle s^2 \rangle$	B−Li	Li−Li	freq. (b_2, a_1, a_1)	ΔE
B3LYP/A	39.72749	1.242	2.317	2.779	269, 288, 430	39.70783	1.305	2.345	2.546	165, 327, 418	12.3
UHF/A	39.44474	1.647	2.349	2.706	303, 329, 451	39.42488	1.664	2.369	2.509	224, 360, 432	12.5
UHF/B	39.45541	1.654	2.326	2.677	297, 332, 449	39.43748	1.672	2.356	2.475	230, 363, 422	11.3
UHF/C	39.45588	1.653	2.327	2.679	296, 332, 448	39.43808	1.671	2.362	2.477	226, 361, 418	11.2
MP2(full)/A	39.50306	1.646	2.333	2.734	292, 334, 452	39.48317	1.664	2.349	2.524	305, 346, 429	12.5
MP2(full)/B	39.55540	1.653	2.309	2.705	289, 338, 450	39.53753	1.671	2.333	2.496	336, 353, 426	11.2
MP2(full)/C	39.55632	1.652	2.309	2.705	289, 338, 450	39.53877	1.670	2.340	2.500	332, 350, 421	11.0
CASSCF(5,5)/A	39.46255	0.750	2.365	2.760	301, 312, 434	39.44271	0.750	2.383	2.574	206, 340, 419	12.5

[a] Total energies in −au, relative energies (ΔE) for the two isomers in kcal/mol, bond lengths in Å, and frequencies in cm^{-1}. [b] A: 6-31G(d), B: 6-311G(d), and C: 6-311+G(d).

TABLE 3: Structural Parameters and Total and Relative Energies for BLi$_3$ Isomers[a]

| | BLi$_3$ (C_{2v}) | | | | | BLi$_3$ (D_{3h}) | | | |
level	energy	B−Li	B−Li	LiBLi′	freq.	energy	B−Li	freq.	ΔE
B3LYP/A	47.27985	2.161	2.270	91.4	109, 184, 211, 417, 462, 616	47.27868	2.155	16i, 198, 403, 582	0.7
B3LYP/B	47.28873	2.146	2.243	91.2	118, 179, 212, 422, 469, 617	47.28725	2.133	23i, 191, 408, 593	0.9
B3LYP/C	47.28902	2.148	2.243	90.2	121, 180, 213, 422, 468, 616	47.28747	2.134	27i, 193, 409, 593	1.0
B3LYP/D	47.28997	2.144	2.236	91.8	117, 180, 212, 422, 471, 615	47.28859	2.130	20i, 191, 410, 594	0.9
HF/A	46.86811	2.183	2.312	97.0	36, 201, 187, 383, 480, 634	46.86836	2.182	69, 211, 411, 587	−0.2
HF/B	46.87871	2.169	2.285	96.8	50, 194, 187, 386, 484, 631	46.87878	2.172	65, 203, 412, 595	0.0
HF/C	46.87908	2.170	2.284	96.8	48, 195, 187, 387, 484, 631	46.87920	2.164	68, 210, 413, 595	−0.1
MP2(full)/A	46.99266	2.178	2.262	94.4	128, 194, 217, 425, 498, 579	46.99094	2.172	30i, 188, 388, 573	1.1
MP2(full)/B	47.05852	2.169	2.236	93.9	124, 180, 213, 427, 514, 594	47.05691	2.160	36i, 176, 403, 585	1.0
MP2(full)/C	47.05969	2.169	2.235	93.9	124, 181, 213, 427, 513, 595	47.05799	2.160	49i, 144, 403, 584	1.1
QCISD/A	47.00746	2.218	2.378	84.1	123, 188, 216, 425, 498, 585	47.00172	2.172	69i, 181, 399, 570	3.6
QCISD/B	47.02444	2.202	2.339	84.2	159, 161, 242, 382, 424, 594	47.01894	2.151	72i, 175, 407, 581	3.5
QCISD/C	47.02539	2.202	2.339	84.2	160, 161, 243, 382, 424, 595	47.01902	2.151	76i, 152, 409, 582	4.0
CASSCF(6,6)/A	46.93623	2.251	2.370	84.9	121, 167, 234, 386, 401, 560	46.93503	2.199	50, 187, 386, 557	0.8

[a] Total energies in −au, relative energies (ΔE) between the two isomers in kcal/mol, bond lengths in Å, angles in degrees, and frequencies in cm^{-1}. [b] A: 6-31G(d), B: 6-311G(d), C: 6-311+G(d), and D: 6-311+G(2df).

TABLE 4: Structural Parameters and Total and Relative Energies for Li$_2$ and Li$_3$ Isomers[a]

| | | | Li$_2$ ($^1\Sigma_g$) | | Li$_3$ ($^2B_2$) | | | | Li$_3$ ($^2A_1$) | | | | |
level	B	Li	energy	Li−Li	energy	$\langle s^2 \rangle$	Li−Li′	Li−Li	energy	$\langle s^2 \rangle$	Li−Li′	Li−Li	ΔE
B3LYP/A	24.65435	7.49098	15.01426	2.723	22.52356	0.784	2.785	3.377	22.52290	0.776	3.094	2.666	0.4
(U)HF/A	24.52203	7.43137	14.86693	2.807	22.31331	1.216	2.868	3.310	22.30987	0.981	3.305	2.719	2.2
(U)HF/B	24.53010	7.43202	14.87035	2.784	22.31841	1.225	2.837	3.253	22.31455	0.983	3.253	2.683	2.4
(U)HF/C	24.53034	7.43203	14.87035	2.784	22.31845	1.226	2.837	3.253	22.31459	0.984	3.253	2.683	2.4
MP2(full)/A	24.56246	7.43186	14.88685	2.773	22.33044	1.183	2.820	3.447	22.33084	0.963	3.152	2.730	−0.3
MP2(full)/B	24.58580	7.44490	14.91512	2.737	22.37277	1.196	2.775	3.368	22.37312	0.967	3.098	2.687	−0.2
MP2(full)/C	24.58631	7.44494	14.91526	2.737	22.37295	1.198	2.780	3.363	22.37331	0.967	3.098	2.687	−0.2
CASSCF/A			14.87792	2.733	22.32036	0.750	2.843	3.313	22.31729	0.750	3.295	2.699	1.9

[a] Total energies in −au, relative energies (ΔE) between the Li$_3$ isomers in kcal/mol, and bond lengths in Å. [b] A: 6-31G(d), B: 6-311G(d), C: 6-311+G(d).

TABLE 5: Total and Relative Energies for BLi, BLi$_2$, and BLi$_3$ Isomers[a]

level[b]	BLi ($^3\Pi_g$)	BLi ($^1\Sigma^+$)	ΔE	BLi$_2$ ($^2B_2$)	BLi$_2$ ($^2B_1$)	ΔE	BLi$_3$ (B_{2v})	BLi$_3$ (B_{3h})	ΔE
CASSCF/6-311+G(2df)//I	32.03663	32.04216	−3.5	39.47439	39.45716	10.8	46.94861	46.94719	0.9
MCQDPT2/6-31G(d)//I	32.04336	32.03601	4.6	39.51922	39.49959	12.3	47.00000	46.99281	4.5
MCQDPT2/6-311+G(2df)//I	32.06879	32.05905	6.1	39.54723	39.53038	10.6	47.03142	47.02602	3.4
QCISD(T)/6-311+G(2df)//II	32.07210	32.06190	6.4	39.55125	39.53416	10.7	47.04795	47.04470	2.0
QCISD(T)/6-311+G(3df)//II	32.07283	32.06268	6.4	39.55206	39.53484	10.8	47.04871	47.04522	2.2
G2	32.07718	32.07270	2.8	39.55958	39.54268	10.6	47.06076	47.05720	2.2
G2(MP2)	32.07709	32.07346	2.3	39.55970	39.54265	10.7	47.06109	47.05712	2.5

[a] Total energies in −au and relative energies (ΔE) between each set of isomers in kcal/mol. [b] I = CASSCF(4,8) for BLi, CASSCF(5,5) for BLi$_2$, and CASSCF(6,6) for BLi$_3$, all using the 6-31G(d) basis set. II = MP2(full)/6-311+G(d).

obtained at G2(MP2). All other methods, including B3LYP/6-31G(d), give similar binding energies (Table 7). Expectantly, these energies are in very good agreement with earlier theoretical estimates.[8,10,13]

BLi$_2$. The $^2B_2$ state with C_{2v} symmetry is the ground state of BLi$_2$. Its energy difference with the $^2B_1$ state is ∼11 kcal/mol. The highest levels of theory (QCI, G2, and MCQDPT2) estimate this $\Delta E(^2B_2 - {}^2B_1)$ to be between 10.6 and 10.8 kcal/mol (Table 5). Larger energy differences of up to 1.7 kcal/mol are found with the smaller 6-31G(d) basis set. B3LYP/6-31G* performs reasonably well, with an energy difference of 12.3 kcal/mol.

The computed atomization energy of BLi$_2$ ($^2B_2$) is estimated at 55.6 kcal/mol at QCI. Both G2 and MCQDPT2 give larger values of 58.4 and 59.0 kcal/mol, respectively. After excluding the empirical correction from the G2 energy, the resulting

TABLE 6: Total and Relative Energies for B, Li, Li_2, and Li_3 Isomers[a]

level[b]	B	Li	Li_2 ($^1\Sigma_g$)	Li_3 ($^2B_2$)	Li_3 ($^2A_1$)	ΔE
CASSCF/6-311+G(2df)//I	24.54626	7.43208	14.87964	22.32743	22.32371	2.3
MCQDPT2/6-31G(d)//I	24.56883	7.43137	14.88779	22.33792	22.33536	1.6
MCQDPT2/6-311+G(2df)//I	24.58667	7.43208	14.89319	22.34735	22.34458	1.7
QCISD(T)/6-311+G(2df)//II	24.59673	7.43203	14.90171	22.35490	22.35454	0.2
QCISD(T)/6-311+G(3df)//II	24.59706	7.43203	14.90154	22.35473	22.35437	0.2
G2	24.60204	7.43222	14.90576	22.35776	22.35737	0.2
G2(MP2)	24.60270	7.43222	14.90640	22.35790	22.35766	0.2

[a] Total energies in -au and relative energies (ΔE) between the two Li_3 isomers in kcal/mol. [b] I = CASSCF(2,8) for Li_2 and CASSCF(5,5) for Li_3, both using the 6-31G(d) basis set. II = MP2(full)/6-311+G(d).

TABLE 7: Atomization Energies (AE) and Reaction Enthalpies for BLi, BLi_2, and BLi_3 Isomers and for Li_2 and Li_3[a]

	BLi ($^3\Pi_g$)	BLi_2 ($^2B_2$)			BLi_3 (C_{2v})					Li_2	Li_3 ($^2B_2$)	
level[b]	AE[c]	AE	(2)	(3)	AE	(5)	(6)	(7)	(8)	AE	AE	(9)
B3LYP/A	27.5	55.8	28.3	36.4	92.8	37.0	46.0	62.0	73.5	19.4	30.8	11.5
MP2(full)/A	22.1	46.7	24.7	32.7	81.6	34.8	45.5	60.7	67.6	14.0	20.9	6.9
MP2(full)/B	24.4	48.6	24.2	33.2	83.7	35.1	43.9	60.8	68.3	15.4	22.9	7.5
MP2(full)/C	24.9	48.8	23.9	33.4	84.0	35.3	43.7	61.1	68.6	15.4	22.9	7.5
MCQDPT2/6-31G(d)//I	20.6	53.5	33.6	38.3	83.3	29.8	48.2	56.9	68.1	15.2	26.4	11.2
MCQDPT2/6-311+G(2df)//I	24.8	59.0	34.0	41.3	90.5	31.5	47.8	59.5	72.8	17.7	31.0	13.3
QCISD(T)/6-311+G(2df)//II	26.4	55.3	28.9	32.1	94.5	39.2	44.9	58.5	71.3	23.2	36.0	12.8
QCISD(T)/6-311+G(3df)//II	26.6	55.6	28.9	32.5	94.8	39.1	45.0	58.9	71.7	23.1	35.9	12.8
G2	26.9	58.4	31.5	32.5	101.7	43.3	48.8	63.4	75.8	25.9	38.3	12.4
G2(MP2)	26.5	58.1	31.6	31.8	101.5	43.4	48.7	63.1	75.2	26.3	38.4	12.1

[a] Energies in kcal/mol. For reactions 1−8 and 9, see text. [b] A: 6-31G(d), B: 6-311G(d), and C: 6-311+G(d). I = CASSCF(4,8) for BLi, CASSCF(5,5) for BLi_2, CASSCF(6,6) for BLi_3, CASSCF(2,8) for Li_2, and CASSCF(5,5) for Li_3, all using the 6-31G(d) basis set. II = MP2(full)/6-311+G(d). [c] Atomization energies.

TABLE 8: Bond Critical Point Data for BLi, BLi_2, and BLi_3[a]

	BLi ($^3\Pi_g$)		BLi_2 ($^2B_2$)				BLi_3 (C_{2v})			
level[b]	ρ(BLi)	$\nabla^2\rho$(BLi)	ρ(BLi)	$\nabla^2\rho$(BLi)	ρ(BLi)	$\nabla^2\rho$(BLi)	ρ(BLi′)	$\nabla^2\rho$(BLi′)		
B3LYP/A	2.81	11.33	2.14	7.46	2.93	11.51	2.25	8.31		
(U)HF/A	3.00	11.77	2.07	7.54	2.96	11.28	2.15	7.17		
(U)HF/B	3.20	12.02	2.23	7.90	3.11	12.02	2.27	8.06		
(U)HF/C	3.18	11.99	2.23	7.91	3.10	12.06	2.27	8.10		
MP2(full)/A	2.90	11.60	2.07	7.48	2.69	10.79	2.29	8.91		
MP2(full)/B	3.12	11.69	2.24	7.87	2.83	11.21	2.45	9.68		
MP2(full)/C	3.10	11.61	2.24	7.89	2.84	11.22	2.46	9.71		
QCISD/A	2.76	11.07			2.63	10.31	1.78	6.31		
CASSCF/A	2.68	10.42	1.96	7.09	2.49	9.47	1.82	6.89		

[a] Electron densities and their Laplacians are in 10^{-2} au. [b] A: 6-31G(d), B: 6-311G(d), C: 6-311+G(d), and D: 6-311+G(2df).

atomization energy of 55.5 kcal/mol is essentially identical to the QCI energy. The NOONs of the active ($^2B_2$) orbitals of the CASSCF(5,5)/6-31G(d) optimized wave function are 1.954 (a_1), 1.582 (a_1), 1.00 (b_2), 0.411 (a_1), and 0.054 (b_1). Similar values are obtained for the $^2B_1$ state. These NOONs are indicative of some configurational mixing and may contribute to the difference in atomization energies obtained between the QCI and MCQDPT2 methods. Again, we find the performance of B3LYP/6-31G(d) to be very satisfactory, with an atomization energy of 55.8 kcal/mol. Interestingly, this and the high level values for BLi_2 ($^2B_2$) are about twice the atomization energy of BLi ($^3\Pi_g$).

Elimination of one Li atom from BLi_2 ($^2B_2$), as in reaction 2, is endothermic by 28.9 kcal/mol at QCI and 5.1 kcal/mol more at MCQDPT2. The G2 dissociation energy of 31.5 kcal/mol is essentially the same as the QCI value after excluding the empirical correction. These B−Li bond dissociation energies are larger than that estimated for BLi ($^3\Pi_g$). Loss of the Li_2 dimer (reaction 3) requires 32.5 kcal/mol as predicted by both QCI and G2, whereas MCQDPT2 estimates this process to be 8.8 kcal/mol more endothermic. At QCI this Li_2 dissociation reaction is nearly isoenergetic, with loss of a single Li atom from BLi_2.

BLi_3. The ground-state structure of BLi_3, with C_{2v} symmetry, has an energy difference with the second-order transition structure (D_{3h}) of only 2.2 kcal/mol at both QCI and G2 and of 3.4 kcal/mol at MCQDPT2 (Tables 3 and 5). These values, except for the one at G2, are reduced upon inclusion of zero-point-energy corrections. Thus, the upper limit for scrambling of the Li atoms in BLi_3 is in the 2−3 kcal/mol range.

The atomization energy of BLi_3 is predicted to be 94.8 kcal/mol at QCI (Table 7). The much larger value of 101.7 kcal/mol obtained with G2 is due to the empirical correction. MCQDPT2 gives a 4.3 kcal/mol lower atomization energy, and the B3LYP/6-31G(d) value of 92.8 kcal/mol is within 2 kcal/mol of the QCI estimate.

Elimination of a single Li atom (reaction 5) is the least endothermic dissociation channel for BLi_3. It requires 39.1 kcal/mol at QCI and 4.2 kcal/mol more at G2 due to the empirical correction, whereas the MCQDPT2 estimate is only 31.5 kcal/mol. At the QCI level, Li elimination from BLi_3 requires 6.6 kcal/mol more than from BLi_2. In contrast, B3LYP/6-31G(d) predicts both reactions 2 and 5 to have similar endothermicities of 37 kcal/mol. Surprisingly, MCQDPT2 gives a 10 kcal/mol larger Li dissociation energy for BLi_2 than for BLi_3.
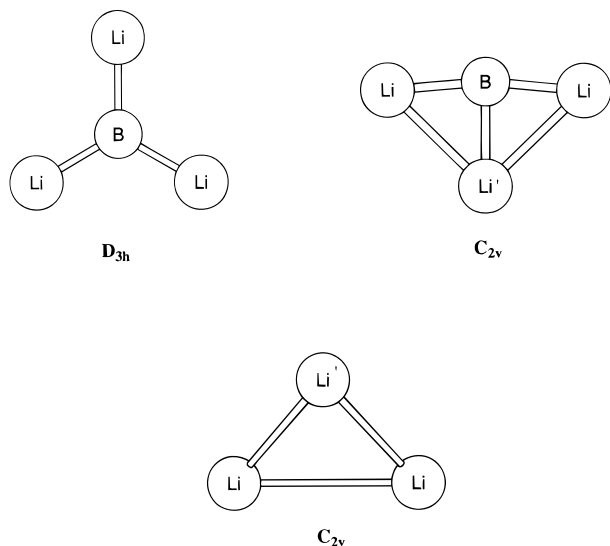
Small Boron−Lithium Clusters

J. Phys. Chem. A, Vol. 102, No. 9, 1998 **1613**

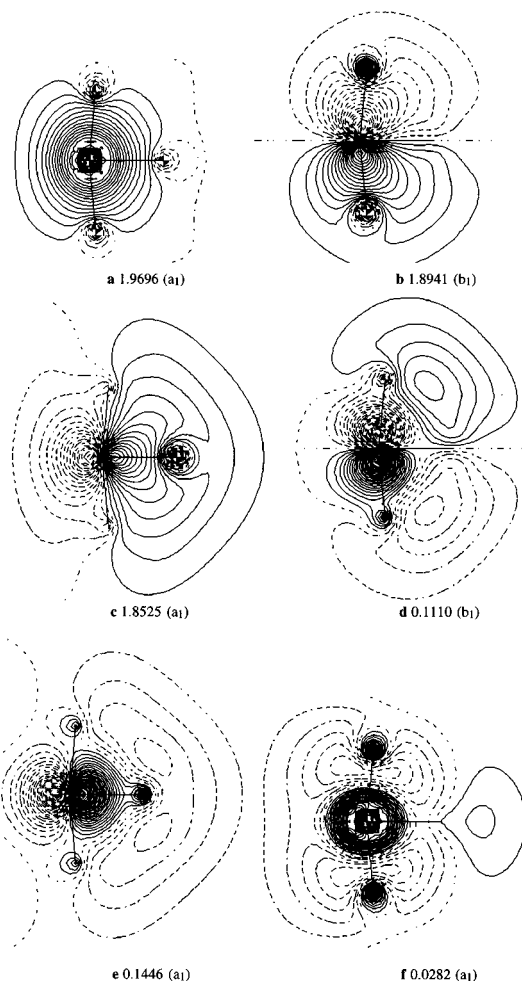**Figure 1.** Structures for BLi$_3$ and Li$_3$.

Figure 2. Active orbitals with occupation numbers for the optimized CASSCF(6,6)/6-31G(*d*) wave function in the σ_v (*xz*) plane of BLi$_3$ (C_{2v}).

Atomic boron elimination from BLi$_3$, producing Li$_3$ in its $^2B_2$ state (reaction 8), requires 71.7 (73.5) kcal/mol at QCI (B3LYP/6-31G(*d*)). This process is significantly more endothermic than the corresponding 32.5 (36.4) kcal/mol needed for elimination of a boron atom from BLi$_2$ (reaction 3). Dissociation of Li$_2$ from BLi$_3$ to give BLi ($^3\Pi_g$), as in reaction 6, requires
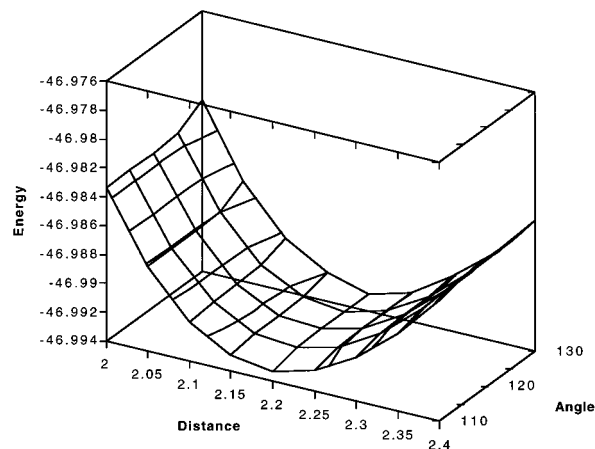
Figure 3. MCQDPT2/6-31G(*d*) potential energy surface for BLi$_3$.

45.0 (46.0) kcal/mol at QCI (B3LYP/6-31G(*d*)). Both reaction 3 and 6 do not appear to be very sensitive to the employed levels of theory. Again, B3LYP performs well.

The atomization energies of both Li$_2$ and Li$_3$ are provided in Table 7 for comparison. With the higher level theoretical models, the atomization energy is constant per Li atom, and amounts to ~13 kcal/mol, in accord with literature estimates.[36] Interestingly, we find that the B−Li and Li−Li binding energies are similar at G2 (26 kcal/mol) with QCI giving a slightly stronger B−Li bond by ~3 kcal/mol. The Li-dissociation energy for Li$_3$ of ~13 kcal/mol (reaction 9) is much smaller than those of 29 and 39 kcal/mol (all QCI) for BLi$_2$ and BLi$_3$, respectively, illustrating the strong influence of the boron atom.

Conclusions

We have examined the structures, harmonic vibrational frequencies, bonding patterns, and reaction enthalpies for all possible dissociation channels of BLi ($^3\Pi_g$), BLi$_2$ ($^2B_2$), and BLi$_3$ (C_{2v}) at several levels of theory with both single reference- and multireference-based correlated methods using a variety of basis sets. Neither of the structures is much influenced by the size of the basis set nor by the method of electron correlation employed. However, dynamic electron correlation is important for characterization of stationary points on the potential energy surface. The D_{3h} symmetry form of BLi$_3$ is a second-order saddle point with an energy difference of 2.2 kcal/mol with the C_{2v} minimum form. Energy evaluations were done at the QCISD(T)/6-311+G(3*df*)//MP2(full)/6-311+G(*d*), MCQDPT2/6-311+G(2*df*)//CASSCF/6-31G(*d*), G2 and G2(MP2) levels of theory. The QCI method gives atomization energies of 27, 56, and 95 kcal/mol for BLi ($^3\Pi_g$), BLi$_2$ ($^2B_2$), and BLi$_3$ (C_{2v}), respectively. After excluding the empirical corrections, the G2 and G2(MP2) energetics are essentially the same as the QCI values. The QCI method estimates the Li-dissociation energies for BLi$_2$ and BLi$_3$ at 29 and 39 kcal/mol, respectively. The same method gives an energy difference of 6.4 kcal/mol for the $^3\Pi_g$ and $^1\Sigma^+$ states of BLi and estimates that the $^2B_2$ state of BLi$_2$ is 10.8 kcal/mol more stable than the $^2B_1$ state. Density functional theory with the hybrid B3LYP functionals using the 6-31G(*d*) basis set performs extremely well. It provides structures, frequencies, and energetics similar in accuracy to the most sophisticated ab initio methods. This result suggests that the B3LYP functionals with the modest 6-31G(*d*) basis set may be an attractive alternative for studying larger boron−lithium clusters.

References and Notes

(1) Davis, S. C.; Klabunde, K. J. *Chem. Rev.* **1982**, *82*, 153.

(2) Koutecký, J.; Fantucci, P. *Chem. Rev.* **1986**, *86*, 539.

(3) Bonacic-Koutecky, V.; Fantucci, P.; Koutecký, J. *Chem. Rev.* **1991**, *91*, 1035.

(4) Meden, A.; Mavri, J.; Bele, M.; Pejovnik, S. *J. Phys. Chem.* **1995**, *99*, 4252.

(5) Kaufman, J. J.; Sachs, L. M. *J. Chem. Phys.* **1970**, *52*, 645.

(6) Cade, P. E.; Huo, W. M. *At. Data Nucl. Data Tables* **1975**, *15*, 1.

(7) Zhu, Z. H.; Murrell, J. N. *Chem. Phys. Lett.* **1982**, *88*, 262.

(8) Knowles, D. B.; Murrell, J. N. *J. Mol. Struct. (Theochem.)* **1986**, *135*, 169.

(9) Saxon, R. P. Theoretical Studies of Boron Compounds; *Proceedings of the High Energy Density Matter*, 1992; Woods Hole, MA.

(10) Sheehy, J. A. Spectroscopy of Lithium Boride, A candidate HEDM Species; *Proceedings of the High Energy Density Matter*, 1995; Woods Hole, MA.

(11) Ivanic, J.; Marsden, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 7503. Marsden, C. J. *J. Chem. Soc., Chem. Commun.* **1989,** 1356. Ivanic, J.; Marsden, C. J.; Hassett, D. M. *J. Chem. Soc., Chem. Commun.* **1993,** 822.

(12) Nemukhin, A. V.; Almlöf, J. *Chem. Phys. Lett.* **1980**, *76*, 601.

(13) Boldyrev, A. I.; Simons, J.; Schleyer, P. v. R. *J. Chem. Phys.* **1993**, *1993*, 8793.

(14) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quant. Chem.* **1981**, *14*, 63.

(15) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* **1981**, *44*, 893.

(16) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893.

(17) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.

(18) Rothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

(19) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1959**, *22*, 571.

(20) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(21) Pople, J. A.; Krishnan, R.; Schlegel, B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 325.

(22) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(23) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(24) Clark, T. C., J.; Spitznagel, G. W., Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(25) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(26) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(27) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(28) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157.

(29) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(30) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(31) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Replogle, E. S. *Chem. Phys. Lett.* **1989**, *158*, 207.

(32) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. B. F.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN94, Revision B.1; Gaussian, Inc.: Pittsburgh, PA, 1994.

(34) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(35) As noted by a referee, this behavior may, in fact, be fortuitous because both states ($^2B_2$ and $^2B_1$) have similar s^2 expectation values.

(36) Boustani, I.; Pewestorf, W.; Fantucci, P.; Bonacic-Koutecký, V.; Koutecký, J. *Phys. Rev. B* **1987**, *35*, 9437.