Aromaticity of Planar B_5^- Anion in the MB_5 (M = Li, Na, K, Rb, and Cs) and MB_5^+ (M = Be, Mg, Ca, and Sr) Clusters

Qian Shu Li* and Qiao Jin

School of Science, Beijing Institute of Technology, Beijing 100081, P. R. China

Received: September 11, 2003; In Final Form: November 20, 2003

The ground-state geometries, electronic structures, and vibrational frequencies of alkali metal−B_5^- MB_5 (M = Li, Na, K, Rb, and Cs) and alkaline earth metal−B_5^- MB_5^+ (M = Be, Mg, Ca, and Sr) clusters were investigated using ab initio self-consistent field and density functional theory (DFT) methods. Calculation results show that planar B_5^- anion can coordinate with the metal atom to form metal−polyboron MB_5 and MB_5^+ species. On the basis of the molecular orbital (MO) analysis and nucleus-independent chemical shifts (NICS), we revealed that the planar B_5^- anion exhibits characteristic of π-aromaticity with two delocalized π electrons and maintains its structural and electronic integrity inside the five MB_5 and four MB_5^+ clusters.

1. Introduction

In 1988, Anderson and co-workers[1] observed the mass distribution of B_n^+ ($n = 1-20$) generated by laser ablation of isotopically pure solid boron. The collision-induced dissociation (CID) results revealed the presence of "magic" $n = 5$ and 13 clusters that exhibited anomalously high intensity. The results of Anderson's group[2−5] inspired theoretical investigation of small bare boron clusters[6−20] and especially B_5 and B_5^+ clusters, whereas a few of theoretical investigations have been reported on the B_5^- cluster. Until recently, we theoretically investigated structures and energetics of neutral, cationic, and anionic B_4[17] and B_5[18] clusters with the MP2/6-311+G* and B3LYP/6-311+G* levels of theory. Zhai et al.[21] investigated the electronic structure and chemical bonding of B_5^- and B_5 using anion photoelectron spectroscopy and ab initio calculations. Excellent agreement between the ab initio detachment energies of the C_{2v} global minimum of B_5^- and the experimental PES spectra firmly established the ground-state structures for both B_5^- and B_5.

The concept of aromaticity has been successfully extended from traditional organic molecules into pure all-metal clusters.[22−31] Li and co-workers[22] presented evidence of aromaticity for MAl_4^- (M = Li, Na, and Cu) purely metallic systems. The Al_4^{2-} dianion in a series of bimetallic clusters was found to have two delocalized π electrons conforming to the $4n + 2$ electron counting rule for aromaticity. Ga_4^{2-} and In_4^{2-} dianions[23] inside the gaseous $NaGa_4^-$ and $NaIn_4^-$ clusters also have similar aromaticity due to the presence of two delocalized π electrons. Li et al.[24] investigated the possibility of aromaticiy in the heterocyclic four-membered ring XAl_3^- (X = Si, Ge, Sn, and Pb) systems and found that the cyclic planar XAl_3^- species have delocalized π electrons and therefore aromaticity. Aromaticity was also proposed in the 10 valence electrons B_3^-, Al_3^-, and Ga_3^- systems to explain the geometrical and electronic properties.[25] Li and Cheng[32] investigated the aromaticity of square planar N_4^{2-} (possessing six delocalized π electrons) in the M_2N_4 (M = Li, Na, K, Rb, or Cs) species. Boldyrev and Wang[33] reported the experimental and theoretical characterization of antiaromaticity in an all-metal system $Li_3Al_4^-$. Molecular orbital analysis revealed that the rectangular Al_4^{4-} tetraanion has four π electrons, consistent with the $4n$ Hückel rule for antiaromaticity.

In the present paper, a series of alkali metal−B_5^- MB_5 (M = Li, Na, K, Rb, and Cs) and alkaline earth metal−B_5^- MB_5^+ (M = Be, Mg, Ca, and Sr) clusters are theoretically investigated using ab initio and DFT methods. We explored the aromaticity of planar B_5^- anion in the five MB_5 and four MB_5^+ species. Molecular orbitals (MO) analysis and the nucleus-independent chemical shifts (NICS) provide insight into the aromaticity of planar B_5^- anion. Our results show that the inorganic B_5^- anion exhibits characteristic π-aromaticity having two delocalized π electrons with structural and magnetic criteria.

2. Computational Methods

All calculations were performed using the Gaussian 98 program package.[34] Equilibrium geometries and vibrational frequencies of B_5^-, MB_5 (M = Li, Na, K, Rb, and Cs), and MB_5^+ (M= Be, Mg, Ca, and Sr) were fully optimized using the B3LYP and MP2 methods, where MP2 stands for the second-order Møller−Plesset perturbation theory,[35] and B3LYP is a DFT method using Becke's three parameter nonlocal exchange functional[36] with the nonlocal correlation functionals of Lee, Yang, and Parr.[37] The 6-311+G* is a split-valence triple-ζ plus polarization basis set augmented with diffuse functions.[35] For the RbB_5, CsB_5, and SrB_5^+ species, we optimized at the B3LYP and MP2 levels of theory, whereas the 6-311+G* basis set was used for boron and the lighter metal atoms and the LANL2DZ basis set was used for the heavier metals Rb ($Z = 37$), Cs ($Z = 55$), and Sr ($Z = 38$). Vibrational frequencies at the above levels were calculated to characterize stationary points as minima (number of imaginary frequencies (NIMAG = 0)) or transition states (NIMAG = 1).

Molecular orbitals (MO) for B_5^-, BeB_5^+, and LiB_5 were calculated by the HF methods with the corresponding basis set. All MO pictures were made using the MOLDEN 3.4 program.[38] NICS values for B_5^- anion, five MB_5, and four MB_5^+ species were calculated with the GIAO-B3LYP//B3LYP method. The natural bond orbital (NBO)[39−42] analysis is also performed to provide insight into the bonding nature and aromaticity of these species.

* Corresponding author. Fax: +86-10-68912665. E-mail: qsli@bit.edu.cn.

10.1021/jp036711b CCC: $27.50
Published on Web 01/08/2004

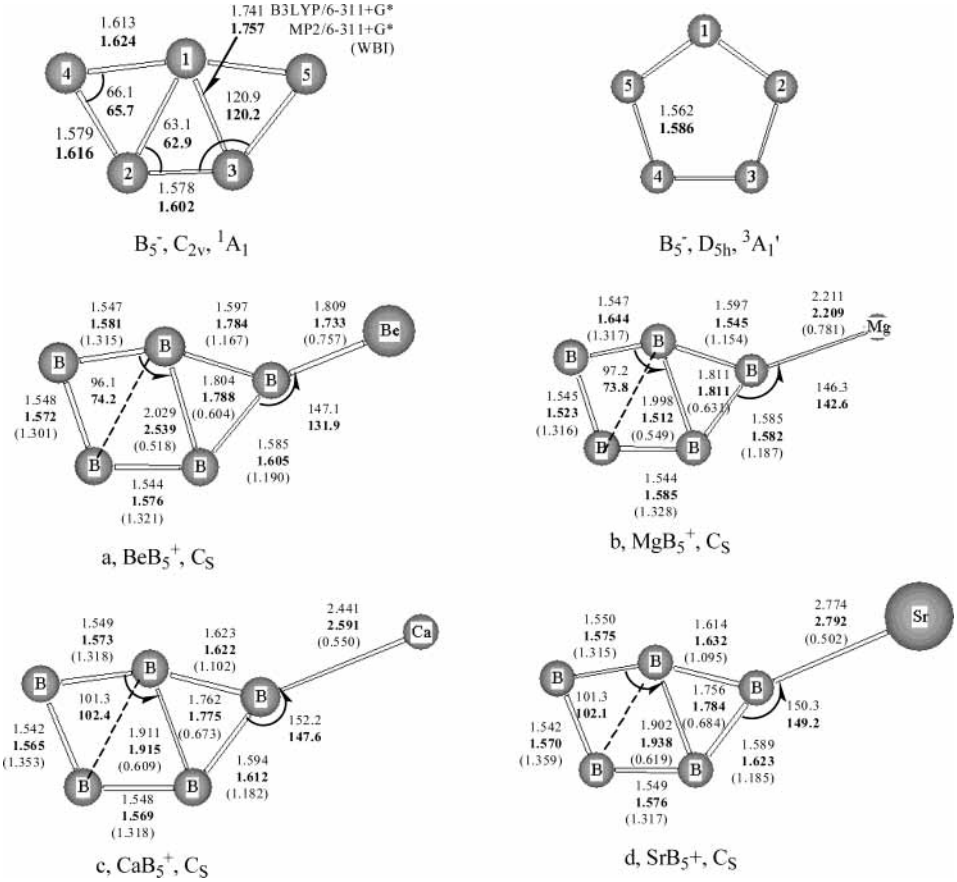

Figure 1. Optimized geometries (bond lengths in ångstroms, bond angles in degrees) and the Wiberg bond indices (WBI) for BeB_5^+, MgB_5^+, CaB_5^+, and SrB_5^+ species at the B3LYP and MP2 (bold font) methods.

3. Results and Discussion

The optimized geometric structures and the Wiberg bond indices (WBI) for B_5^- anion, five MB_5, and four MB_5^+ species were shown in Figures 1 and 2. Total energies, ZPE, and the number of imaginary frequencies of all species are summarized in Table 1. The calculated average bond lengths (in Å), covalent radii (in Å), and zero-point corrected B3LYP energies (in kcal/mol) for hypothetical reactions $MB_5 \rightarrow M + B_5$ or $MB_5^+ \rightarrow M^+ + B_5$ are listed in Table 2. The harmonic vibraional frequencies of B_5^-, five MB_5, and four MB_5^+ species at the B3LYP method are shown in Table 3. The calculated NICS values are given in Table 4. MOs pictures for B_5^-, BeB_5^+, and LiB_5 are exhibited in Figure 3.

3.1. Geometric Structures and Optimized Bond Lengths. Extensive searches were carried out for the most stable structure of B_5^- at the B3LYP/6-311+G* and MP2/6-311+G* levels of theory. Theoretical studies on various B_5^- anions showed that a C_{2v} planar five-membered ring structure is the global minimum of B_5^-, in good agreement with previous results.[18,21] The most stable structure of the B_5^- anion (C_{2v}, $^1A_1$) is a Jahn−Teller distorted pentagon. To understand this distortion, the triplet B_5^- structure with the D_{5h} symmetry must be considered. The pentagonal B_5^- anion (D_{5h}, $^3A_1'$) is a second-order saddle point at the B3LYP/6-311+G* level of theory, whereas it is a local minima at the MP2/6-311+G* level of theory. The triplet B_5^- (D_{5h}) anion is energetically higher than the most stable B_5^- anion (C_{2v}, $^1A_1$) by 87.1 kcal/mol at the MP2/6-311+G* level of theory (shown in Table 1).

We performed ab initio and DFT methods on a wide variety of metal−polyboron clusters and found that all the ground-state MB_5 and MB_5^+ geometries are local minima with all real frequencies at the B3LYP and MP2 levels of theory. The metal atoms are lying in the five-membered ring plane bound to a boron atom of the five-membered ring. Planar B_5^- anion can

TABLE 1: Total Energies (*E*),[a] Zero-Point Energies (ZPE),[b] and the Number of Imaginary Frequencies (NIMAG) for B_5^-, MB_5^+, and MB_5 Species[c−e]

species		B3LYP		MP2		
		E[a]	ZPE[b]	E[a]	ZPE[b]	RE[f]
B_5^-	C_{2v}, $^1A_1$	−124.080871	9.8(0)	−123.619033	9.7(0)	0.0
B_5^-	D_{5h}, $^3A_1'$	−123.973339	8.4(2)	−123.480303	29.3(0)	87.1
BeB_5^+	C_s	−138.456963	11.4(0)	−137.929887	11.4(0)	0.0
	C_{5v}			−137.778721	11.7(2)	94.8
MgB_5^+	C_s	−323.879458	10.9(0)	−322. 835606	9.8(2)	0.0
	C_{5v}			−322.896608	11.2(0)	−38.3
CaB_5^+	C_s	−801.412904	10.7(0)	−800.094010	10.8(0)	0.0
	C_{5v}	−801.361058	9.8(2)	−800.024951	11.9(0)	43.3
SrB_5^+	C_s	−154.261629	10.7(0)	−153.507621	10.4(0)	0.0
	C_{5v}	−154.182747	9.4(2)	−153.435802	12.1(0)	45.1
LiB_5	C_s	−131.564901	10.1(0)	−131.014821	10.9(0)	0.0
	C_{5v}	−131.503173	10.2(2)	−130.985829	12.8(0)	18.2
NaB_5	C_s	−286.342692	10.6(0)	−285.446434	10.3(0)	0.0
	C_{5v}	−286.268458	9.5(2)	−285.372411	13.6(0)	46.5
KB_5	C_s	−723.984892	10.5(0)	−722.923548	10.5(0)	0.0
	C_{5v}	−723.912690	9.3(2)	−722.856391	14.9(0)	42.1
RbB_5	C_1	−147.914809	10.5(0)	−147.188303	10.3(0)	0.0
	C_{5v}	−147.838185	9.1(2)	−147.100024	17.4(0)	55.4
CsB_5	C_{2v}	−143.931687	10.3(0)	−143.179111	10.5(0)	0.0
	C_{5v}	−143.852969	9.0(2)	−143.123015	19.2(0)	35.2

[a] Total energies in Hartree. [b] Zero-point energies in kcal/mol. [c] The integers in parentheses are the number of imaginary frequencies (NIMAG). [d] The listed toatal energies for MB_5^+ and MB_5 species at the B3LYP and MP2 methods. [e] The 6-311+G* basis set was used for boron, and the LANL2DZ basis set was used for Sr, Rb, and Cs. [f] Relative energies (in kcal/mol) for B_5^-, MB_5^+, and MB_5 species (C_s and C_{5v}) at the MP2 method.

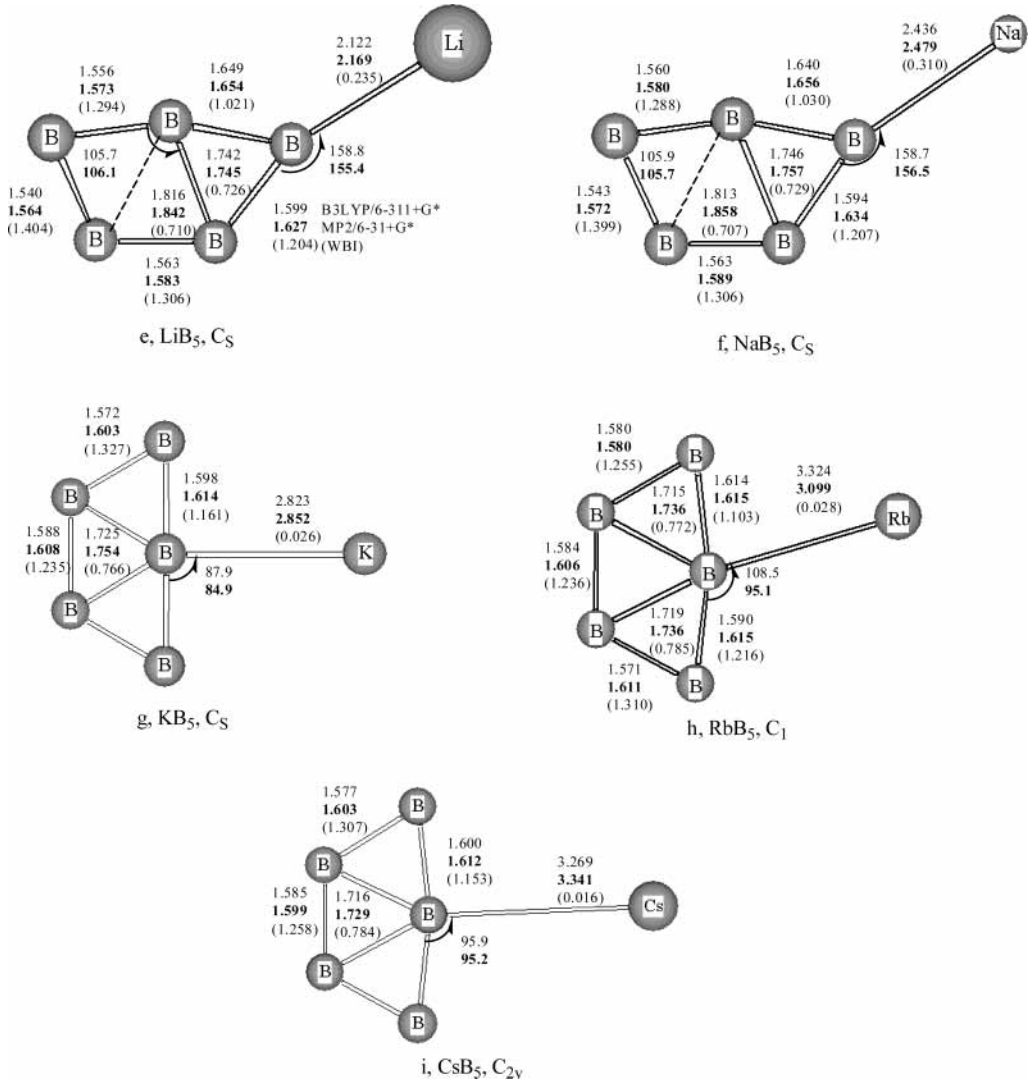

Figure 2. Optimized geometries (bond lengths in ågstroms, bond angles in degrees) and the Wiberg bond indices (WBI) for LiB_5, NaB_5, KB_5, RbB_5, and CsB_5 species at the B3LYP and MP2 (bold font) methods.

TABLE 2: Calculated Bond Lengths (in Å), Covalent Radii (in Å), and Zero-Point Corrected B3LYP Energies (in kcal/mol) for Hypothetical Reactions $MB_5^+ \rightarrow M^+ + B_5$ or $MB_5 \rightarrow M + B_5$

species	BeB_5^+	MgB_5^+	CaB_5^+	SrB_5^+	LiB_5	NaB_5	KB_5	RbB_5	CsB_5
B−B	1.564	1.564	1.571	1.569	1.581	1.580	1.586	1.588	1.588
M−B	1.809	2.211	2.441	2.774	2.122	2.436	2.823	3.324	3.269
sum of covalent radii	1.77	2.25	2.62	2.79	2.10	2.45	2.90	3.04	3.23
ΔE	73.8	42.1	37.6	28.7	44.3	33.2	34.9	30.3	32.3

coordinate with a metal atom to form metal−polyboron compounds MB_5 and MB_5^+. Five MB_5 and four MB_5^+ species possess planar or quasi-planar structures containing the metal cation interacting with a planar B_5^- unit. Nine species have C_s symmetry except for the RbB_5 (C_1) and CsB_5 (C_{2v}) species.

In addition, we also have calculated the pentagonal pyramid structures MB_5 and MB_5^+ (C_{5v}, $^3A_1$) geometries. The triplet C_{5v} MB_5^+ (M = Mg, Ca, and Sr) clusters are local minima at the MP2/6-311+G* level of theory. The triplet C_{5v} MB_5 (M = Li, Na, K, Rb, and Cs) clusters are second-order saddle points at the B3LYP/6-311+G* level of theory and local minima at the MP2/6-311+G* level of theory. They are energetically higher than the ground-state MB_5 and MB_5^+ geometries at the B3LYP /6-311+G* and MP2/6-311+G* levels of theory (shown in Table 1).

As shown in Figures 1 and 2, the bond lengths of B−B in the five MB_5 and four MB_5^+ species are slightly different using the B3LYP and MP2 methods. The B−B bond lengths (1.540−1.754 Å) in the five MB_5 and four MB_5^+ species are much shorter than the sum of covalent radii of boron (1.76 Å),

TABLE 3: Calculated Vibrational Frequencies (in cm^{-1}) for the B_5^-, MB_5^+, and MB_5 Species

	B3LYP								
species	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8	ω_9
B_5^- (C_{2v} $^1A_1$)	253	374	581	638	718	964	997	1066	1258
BeB_5^+	124	142	238	335	380	535	663	757	1017
MgB_5^+	101	116	261	317	332	368	643	764	986
CaB_5^+	63	88	269	332	351	363	696	711	976
SrB_5^+	45	79	207	325	353	361	690	716	968
LiB_5	76	106	324	376	452	484	648	750	964
NaB_5	56	89	255	318	373	491	662	729	957
KB_5	56	64	208	292	386	604	682	748	988
RbB_5	48	96	159	247	387	618	664	747	991
CsB_5	38	54	129	246	388	618	662	751	994

[a] The 6-311+G* basis set was used for B, Be, Mg, Ca, Li, Na, and K, and the LANL2DZ basis set was used for the heavier metals Sr, Rb, and Cs.

TABLE 4: NICS Values (in ppm) for the B_5^-, MB_5^+, and MB_5 Species Calculated at the GIAO−B3LYP//B3LYP Method

species	benzene	B_5^- (C_{2v})	BeB_6^+	MgB_6^+	CaB_6^+	SrB_6^+	LiB_5	NaB_5	KB_5	RbB_5	CsB_5
NICS (0.0)[a]	−10.13	−7.01	−17.59	−18.53	−15.04	−14.91	−9.98	−9.68	−14.98	−7.22	−5.50
NICS (0.5)[b]	−11.28	−15.14	−19.68	−20.41	−18.85	−18.81	−15.83	−15.66	−24.37	−6.82	−14.23

[a] NICS (0.0), calculated NICS values at the geometric center of the five-membered ring. [b] NICS (0.5), calculated NICS values above (by 0.5 Å) the geometric centers of the five-membered ring.

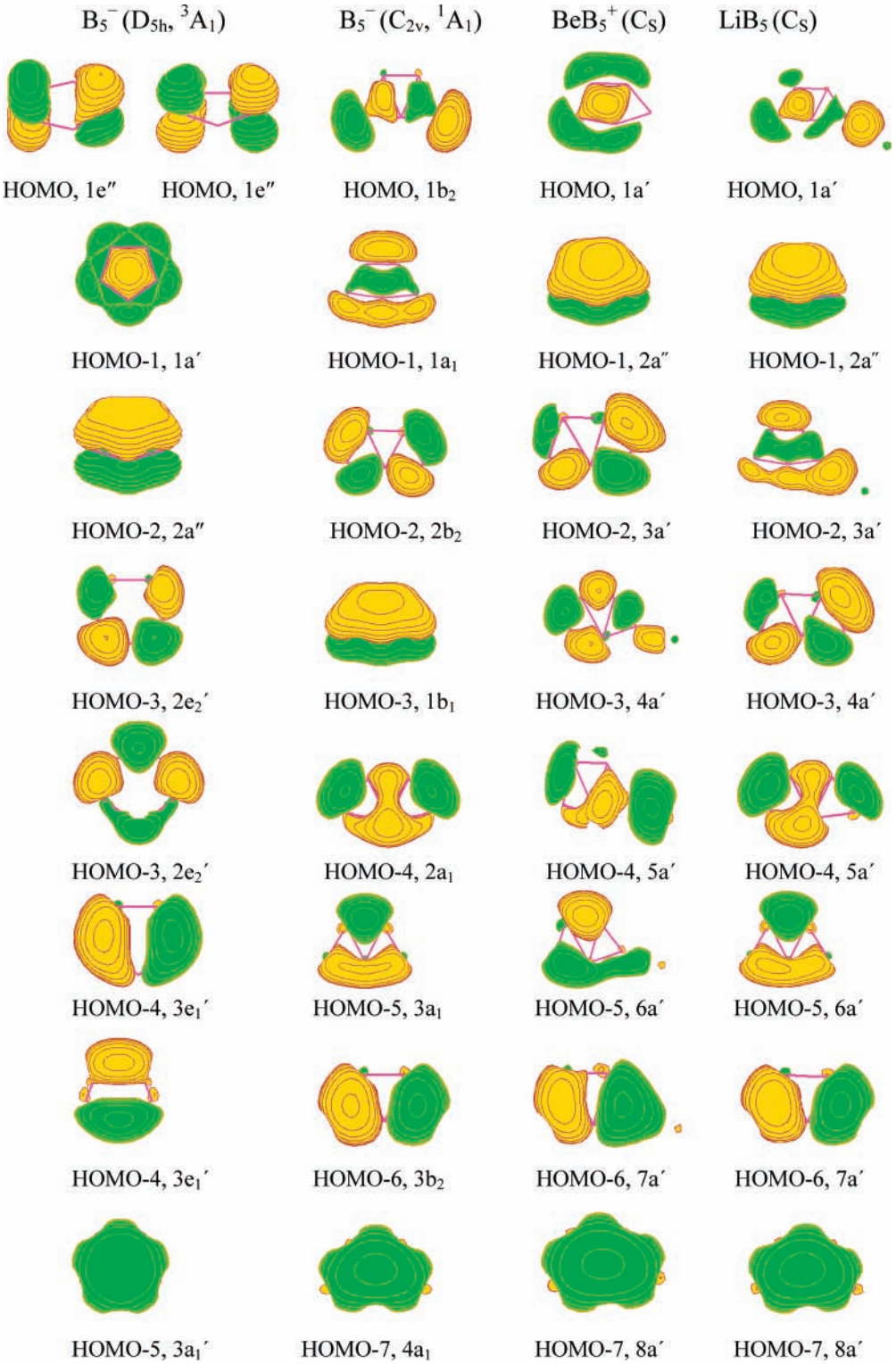

Figure 3. Molecular orbital pictures for the B_5^- anion, BeB_5^+, and LiB_5 species.

supporting the existing stronger B−B bonding. The M−B bond lengths in the five MB_5 and four MB_5^+ species are very close to the sum of covalent radii of the corresponding metal atoms and boron atom except for CaB_5^+, KB_5, and RbB_5. The covalent radii for the metal atoms and boron atom were assumed to be 0.89, 1.37, 1.74, 1.91, 1.22, 1.57, 2.02, 2.16, 2.35, and 0.88 Å for Be, Mg, Ca, Sr, Li, Na, K, Rb, Cs, and B, respectively.[43] The calculated averaged bond lengths in the five-membered ring

for the MB_5^+ and MB_5 species are clearly shorter than the calculated average bond length (1.592 Å) in the most stable planar B_5^- (C_{2v}) unit (shown in Table 2).

Figures 1 and 2 show that the B_5^- anion preserves its planar five-membered ring structural integrity in forming the MB_5 (M = Li, Na, K, Rb, and Cs) and MB_5^+ (M = Be, Mg, Ca, and Sr) species. Although in the five MB_5 and four MB_5^+ species, the structure of the B_5^- anion is somewhat distorted from a perfect planar five-membered ring (C_{2v}), the distortion is very modest and the geometric integrity of the B_5^- anion is easily recognizable. Furthermore, the bond lengths of the five-membered ring are almost identical, suggesting the aromaticity of the planar B_5^- anion with structural criteria.

3.2. Natural Population Analysis and Vibrational Frequencies. In terms of natural population analysis, all positive charge mainly lies on the metal atoms and all negative charge populates on the boron atoms. The MB_5 and MB_5^+ clusters can be regarded as complexes of the B_5^- anion with the metal cations. Bonding was found to be quite ionic between the metal and B_5^-: Q(Be) = +1.31 e (BeB_5^+), Q(Mg) = +1.27 e (MgB_5^+), Q(Ca) = +1.62 e (CaB_5^+), and Q(Sr) = +1.66 e (SrB_5^+) (all are computed at the B3LYP/6-311+G* level). With increasing atom number, the positive charges are mainly located over the metal atoms. Natural population analysis show that Q(Li) = +0.85 e (LiB_5), Q(Na) = +0.80 e (NaB_5), Q(K) = +0.99 e (KB_5), Q(Rb) = +0.99 e (RbB_5), and Q(Cs) = +1.00 e (CsB_5). At the same time, the WBI between the metal atom and boron atom in the LiB_5, NaB_5, KB_5, RbB_5, and CsB_5 are 0.235, 0.310, 0.026, 0.028, and 0.016, respectively. The very high ionic character in the chemical bonds of these clusters is obvious. The B_5^- anion might be stabilized as the planar five-membered ring by the interaction of its π system with the metal atoms. However, the metal cations have strong influences on the electronic structure of the B_5^- anion for the heavier metal atoms. So, RbB_5 and CsB_5 systems might change into the nonplanar structure that the five boron atoms and metal atoms are not in a plane.

The calculated harmonic vibrational frequencies at the B3LYP method for the five MB_5 and four MB_5^+ species are given in Table 3. The lowest vibrational frequencies calculated are large enough to prove the minimum. Whichever theoretical method was chosen, B3LYP or MP2, it made no significant difference to the vibrational frequencies for the five MB_5 and four MB_5^+ species.

3.3. Aromaticity of Planar B_5^- Anion. *3.3.1. Stabilities of the Five MB_5 and Four MB_5^+ Species.* The zero-point corrected B3LYP energies for hypothetical reactions $MB_5 \rightarrow M + B_5$ (M = Li, Na, K, Rb, and Cs) and $MB_5^+ \rightarrow M^+ + B_5$ (M = Be, Mg, Ca and Sr) are given in Table 2. The MB_5^+ (M = Be, Mg, Ca and Sr) species lie about 28.7−73.8 kcal/mol above the energy of the ground-state alkaline earth metal cations M^+ and the planar B_5 (C_{2v}) cluster using the B3LYP method. The MB_5 (M = Li, Na, K, Rb, and Cs) species lie about 30.3−44.3 kcal/mol above the energy of a ground-state alkali metal atoms and the planar B_5 (C_{2v}) cluster at the B3LYP method. Reactions are all endothermic, indicating that the MB_5 and MB_5^+ species are stable toward decomposition. Among the nine species, the BeB_5^+ species is the most stable one because the reaction needs the largest energies. A simple comparison of the MB_5^+ or MB_5 and the planar B_5 cluster energies shows a substantial energy stabilization of the MB_5^+ and MB_5 species.

3.3.2. Nucleus-Independent Chemical Shifts (NICS). Aromaticity is often discussed in terms of various criteria such as energetic, magnetic, and geometric.[44−46] NICS (nucleus-independent chemical shift), proposed by Schleyer and coworkers,[46] is based on magnetic shieldings, which have long been calculated by simple methods,[47] and now can be computed with a modern ab initio technique.[48] NICS are computed at selected points inside or around molecules, typically at ring centers and above. Aromaticity is characterized by negative NICS values, antiaromaticity by positive NICS, and nonaromatic compounds by values close to zero.

In this study we first calculated NICS (0.0) at the geometrical centers of the planar five-membered ring, which provide a direct measure of the ring current effects. The calculated results are listed in Table 4. For the planar five-membered B_5^- structure, the NICS value of −7.01 ppm computed at the center of the five-membered ring suggests that this anionic B_5^- unit is aromatic. NICS values of the nine species are all negative and larger than that of the B_5^- unit. To further analyze the aromaticity, we calculated the NICS (0.5) values by placing a ghost atom above (by 0.5 Å) the centers of the five-membered ring. NICS (0.0) and NICS (0.5) for the nine species are all negative, supporting the existence of delocalization and aromaticity of the B_5^- anion in these nine species. We found that NICS (0.0) and NICS (0.5) values for the MB_5^+ (M = Mg, Ca, and Sr) species decrease with increasing atomic number of the metal, indicating the decreasing of the aromaticity of MgB_5^+, CaB_5^+, and SrB_5^+ species. According to the NBO analysis, the calculated adjacent B−B WBI in the five-membered ring for B_5^-, MB_5, and MB_5^+ species are in the range 1.1−1.3, which are between the standard values of single-bond (1.0) and double-bond (2.0), indicating the existence of delocalization.

3.3.3. Molecular Orbital Analysis. As exhibited in Figure 3, the highest occupied MO (HOMO, $1b_2$) of the planar B_5^- (C_{2v}, $^1A_1$) anion is a bonding orbital within the triangular wings B1−B2−B4 and B1−B3−B5 (Figure 1). The HOMO−1 ($1a_1$) is formed from the in-plane p orbital and it is the peripheral four-center σ-bonding MO. The HOMO−2 ($2b_2$) is σ-bonding MO formed from the in-plane p orbitals. Clearly the HOMO−3 ($1b_1$), which is formed from the out-of-plane p orbitals of the five boron atoms, is a delocalized π-bonding MO, which renders π-aromaticity. The following three MOs are formed primarily from the s and p orbitals. The HOMO-7 ($4a_1$) is a sum of the s orbitals of the five boron atoms. Among these occupied orbitals, the HOMO-3 ($1b_1$) is a delocalized π-bonding MO, containing two π electrons. The two delocalized π electrons give the agreement with the $4n + 2$ electron counting rule. Certainly, the presence of the delocalized π orbital plays an important role in the stabilization of this metal-polyboron species. Furthermore, B_5^- has a perfect planar (C_{2v}) structure, due to the delocalization of π electrons, exactly as expected for an aromatic system.

To understand the electronic structure of the most stable B_5^- (C_{2v}, $^1A_1$) anion, we should study the electronic structure of the pentagonal B_5^- (D_{5h}, $^3A_1'$) isomer. Figure 3 shows the nine valence MOs for the pentagonal B_5^- (D_{5h}, $^3A_1'$) isomer. This triplet state is a highly symmetric pentagon with D_{5h} symmetry. As soon as the degenerate orbitals for the triplet state B_5^- (D_{5h}) isomer are partially occupied, the Jahn−Teller distortion occurs and leads to a symmetry lowering from D_{5h} into C_{2v}. Meanwhile, the deformation causes a splitting of the degenerate orbitals transforming from e″ into a_2 and b_2 levels.

MO pictures for C_{2v} and D_{5h} B_5^- isomers show that the key orbital is HOMO−1 (Figure 3). For the singlet B_5^- with C_{2v} symmetry, the HOMO−1 ($1a_1$) represents the peripheral four-center bond and the $1a_1$ orbital is a strong bonding MO;[21] for triplet B_5^- with D_{5h} symmetry, the HOMO−1 (1a′) represents

the peripheral five-center bond and is the only completely σ-delocalized molecular orbital to be called σ-aromatic.

Figure 3 also shows the eight valence MOs for BeB_5^+ and LiB_5. The canonical MO ordering of BeB_5^+ and LiB_5 is different from that of B_5^-. In the BeB_5^+ and LiB_5 species the MOs of the B_5^- anion can be easily recognized. They only distort slightly by the presence of the metal cations, exhibiting the electronic integrity of the B_5^- anion. We found that a similar delocalized π orbital and the peripheral four-center bond are also present in the BeB_5^+ and LiB_5 species, showing the electronic integrity of the B_5^- anion. The other MB_5^+ and MB_5 species also have similar MO pictures.

Molecular orbital analysis for the B_5^- anion revealed an interesting and delocalized π MO. They contribute the property of the π-aromaticity for the B_5^- anion, due to the presence of two π electrons which follow the $4n + 2$ electron counting rule.

4. Conclusion

In this paper, the equilibrium geometries and harmonic vibrational frequencies of the low-lying states of alkali metal$-B_5^-$ MB_5 (M = Li, Na, K, Rb, and Cs) and alkaline earth metal$-B_5^-$ MB_5^+ (M = Be, Mg, Ca, and Sr) clusters are discussed for the first time. Comprehensive calculations show that the planar B_5^- anion can coordinate with one metal atom to form MB_5 and MB_5^+. First, the presence of two delocalized π electrons of B_5^- anion satisfies the $4n + 2$ electron counting rule, exhibiting characteristics of π-aromaticity for the B_5^- anion. Second, B_5^- has a planar five-member ring structure, due to the delocalized π electrons. Third, NICS and WBI values suggest the property of aromaticity of the B_5^- anion. Finally, the structural and electronic integrity of the B_5^- anion inside the MB_5^+ and MB_5 species can be presented. Therefore, the planar cyclic B_5^- anion exhibits characteristics of π-aromaticity and maintains its structural and electronic integrity inside of the MB_5 and MB_5^+ species. These findings are significant for expanding the aromaticity concept into inorganic B_5^- cluster.

References and Notes

(1) Hanley, L.; Whitten, J. L.; Anderson, S. L. *J. Phys. Chem.* **1988**, *92*, 5803.
(2) Ruatta, S. A.; Hanley, L.; Anderson, S. L. *J. Chem. Phys.* **1989**, *91*, 226.
(3) Hintz, P. A.; Ruatta, S. A.; Anderson, S. L. *J. Chem. Phys.* **1990**, *92*, 292.
(4) Ruatta, S. A.; Hintz, P. A.; Anderson, S. L. *J. Chem. Phys.* **1991**, *94*, 2833.
(5) Hintz, P. A.; Sowa, M. B.; Ruatta, S. A.; Anderson, S. L. *J. Chem. Phys.* **1991**, *94*, 6446.
(6) Bruna, P. J.; Wright, J. S. *J. Phys. Chem.* **1990**, *94*, 1774; *J. Mol. Struct.* **1990**, *210*, 243; *J. Chem. Phys.* **1989**, *91*, 1126; *J. Chem. Phys.* **1990**, *93*, 2617.
(7) Niu, J.; Rao, B. K.; Jena, P. *J. Chem. Phys*. **1997**, *107*, 132.
(8) Langhoff, S. R.; Bauschlicher, C. W. *J. Chem. Phys*. **1991**, *95*, 5882.
(9) Kimura, K.; Takeda, M.; Fujimori, M.; Tamura, R.; Matsuda, H.; Schmechel, R.; Werheit, H. *J. Solid State Chem*. **1997**, *133*, 302.
(10) Hernandez, R.; Simons, J. *J. Chem. Phys*. **1991**, *94*, 2961.
(11) Ray, A. K.; Howard, I. A.; Kanal, K. M. *Phys. Rev. B* **1992**, *45*, 14247.
(12) Kato, A. U.; Yamashita, K.; Morokuma, K. *Chem. Phys. Lett*. **1992**, *190*, 361.
(13) Boustani, I.*Surf. Sci*. **1996**, *370*, 355; *Int. J. Quantum Chem*. **1994**, *52*, 1081; *Chem. Phys. Lett.* **1995**, *233*, 273; *Chem. Phys. Lett.* **1995**, *240*, 135; *Phys. Rev. B* **1997**, *55*, 16426.
(14) Tang, A. C.; Li, Q. S. *Int. J. Quantum Chem*. **1986**, *29*, 579.
(15) Tang, A. C.; Li, Q. S.; Liu, C. W.; Li, J. *Chem. Phys. Lett.* **1993**, *201*, 465.
(16) Li, Q. S.; Gu, F. L.; Tang, A. C. *Int. J. Quantum Chem*. **1994**, *50*, 173.
(17) Jin, H. W.; Li, Q. S. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1110.
(18) Li, Q. S.; Jin, H. W. *J. Phys. Chem. A* **2002**, *106*, 7042.
(19) Alexandrova, A. N.; Boldyrev, A. I.; Zhai, H. J.; Wang, L. S.; Steiner, E.; Fowler, P. W. *J. Phys. Chem. A* **2003**, *107*, 1359.
(20) Ma, J.; Li, Z. H.; Fan, K. N.; Zhou, M. F. *Chem. Phys. Lett.* **2003**, *372*, 708.
(21) Zhai, H. J.; Wang, L. S.; Alexandrova, A. N.; Boldyrev, A. I. *J. Chem. Phys*. **2002**, *117*, 7917.
(22) Li, X.; Kuznetsov, A. E.; Zhang, H. F.; Boldyrev, A. I.; Wang, L. S. *Science* **2001**, *291*, 859.
(23) Kuznetsov, A. E.; Boldyrev, A. I.; Li, X.; Wang, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 8825.
(24) Li, X.; Zhang, H. F.; Wang, L. S.; Kuznetsov, A. E.; Cannon, N. A.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 1867.
(25) Kuznetsov, A. E.; Boldyrev, A. I. *Struct. Chem*. **2002**, *13*, 141.
(26) Alexandrova, A. N.; Boldyrev, A. I. *J. Phys. Chem. A* **2003**, *107*, 554.
(27) Kuznetsov, A. E.; Wang, L. S.; Corbett, J. D.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 3369.
(28) Boldyrev, A. I.; Kuznetsov, A. E. *Inorg. Chem*. **2002**, *41*, 532.
(29) Kuznetsov, A. E.; Boldyrev, A. I.; Zhai, H. J.; Li, X.; Wang, L. S. *J. Am. Chem. Soc.* **2002**, *124*, 11791.
(30) Li, X.; Wang, L. S.; Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1999**, *121*, 6033.
(31) Wang, L. S.; Boldyrev, A. I.; Li, X.; Simons, J. *J. Am. Chem. Soc.* **2000**, *122*, 7681.
(32) Kuznetsov, A. E.; Alexander Birch, K.; Boldyrev, A. I.; Li, X.; Zhai H. J.; Wang, L. S. *Sience* **2003**, *300*, 622.
(33) Li Q. S.; Cheng L. P. *J. Phys. Chem. A* **2003**, *107*, 2882.
(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
(35) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.
(36) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(37) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(38) Schaftenaar, G. MOLDEN 3.4, CAOS/CAMM Center, The Netherlands. 1998.
(39) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41.
(40) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc*. **1980**, *102*, 7211.
(41) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(42) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys*. **1985**, *83*, 735.
(43) *Periodic Table of Elements*; Wiley-VCH: Weinheim, 1997.
(44) Schleyer, P. v. R.; Subramanian, G.; Jiao, H.; Najafian, K.; Hofmann, M. *In Advances in Boron Chemistry*; Siebert, W., Eds.; Royal Society of Chemistry: Cambridge, U.K., 1997; p 1−14.
(45) (a) Schleyer, P. v. R.; Najafian, K. Are Polyhedral Boranes, Carboranes, and Carbocations Aromatic? In *The Borane, Carborane, Carbocation Continuum*; Casanova, J., Ed.; Wiley: New York, 1998; pp 169−190. (b) Schleyer, P. v. R.; Najafian, K. *Inorg. Chem.* **1998**, *37*, 3454.
(46) (a) Hofmann, M.; Schleyer, P. v. R. *Inorg. Chem.* **1999**, *38*, 652. (b) Unverzagt, M.; Winkler, H. J.; Brock, M.; Hofmann, M.; Schleyer, P. v. R.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 853. (c) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.
(47) Pasquarello, A.; Schlüter, M.; Haddon, R. C. *Science* **1992**, *257*, 1660.
(48) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.