Novel Pyramidal MB_7 (M = Li, Na, K, Rb, or Cs) Species: Structure and Aromaticity

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The structures and stabilities of a series of pyramidal MB_7 (M = Li, Na, K, Rb, Cs) species were studied by using ab initio (MP2/6-311+G*) and density functional theory (B3LYP/6-311+G* and B3PW91/6-311+G*) methods. It is found that most MB_7 species (except RbB_7 and CsB_7 at the MP2 level) are minima at the C_{7v} symmetric structure, which corresponds to a complex of an M^+ cation with a planar heptagonal B_7^- ring. Nucleus-independent chemical shift and molecular orbital analyses confirm that the planar heptagonal B_7^- ring exhibits aromatic nature. The stabilization of the planar B_7^- ring is mainly attributed to the electrostatic interaction.

1. Introduction

Aromaticity usually refers to benzene and relevant organic compounds which have specific stability and possess $(4n + 2)$ π electrons. The concept of aromaticity has been extended to heterosystems[1−4] and organometallic species.[5−7] Recently, the purely metallic MAl_4^- (M = Li, Na, or Cu)[8] and gaseous $NaGa_4^-$ and $NaIn_4^-$ systems[9] were studied and found to have two delocalized π electrons and thus aromaticity. Aromaticity was also found in heterosystems XAl_3^- (X = Si, Ge, Sn, and Pb)[10] and 10-valence-electron X_3^- (X = B, Al, Ga) systems.[11] Besides, Boldyrev et al. confirmed the specific stability of the planar square Hg_4^{6-} cluster in the Na−Hg amalgams by using the multifold aromaticity concept.[12] Alexandrova and Boldyrev discussed σ aromaticity of the small alkali-metal and alkaline-earth-metal clusters and the specific stabilities of Li_3^+ and Li_3^- ions.[13]

There are many reports on the B_n clusters in experimental and theoretical studies. Alexandrova et al.[14] and Zhai et al.[15] investigated the electronic structures and chemical bonding of B_6^- and B_6[14] and B_5^- and B_5[15] using anion photoelectron spectroscopy and ab initio calculation. Ma et al. studied the geometry, chemical bonding, and aromaticity of B_6, B_6^+, B_6^-, and B_6^{2-} isomers using the B3LYP/6-31+(G) density functional theory (DFT) method.[16] Our group performed theoretical studies on B_4, B_4^+, and B_4^- isomers with ab initio and DFT methods[17] and predicted the structures and stabilities of B_5, B_5^+, and B_5^- with the B3LYP/6-311+G* and MP2/6-311+G* methods.[18] We also investigated the stabilities of B_6, B_6^+, and B_6^- isomers at the HF/6-311(+)G*, B3LYP/6-311(+)G* and MP2/6-311(+)G* levels of theory.[19] It is reported that octahedron the B_6 unit in metal polyboron compounds[20−22] is the common building block. In addition to the B_n clusters, our group[23] has also investigated aromaticity for pyramidal MB_6 (M = Be, Mg, Ca, and Sr) clusters. In the present work, we study the structure and stability for the pyramidal alkali-metal−B_7 (MB_7) (C_{7v} symmetry) (M = Li, Na, K, Rb, or Cs) systems.

2. Computational Methods

Geometry optimization and vibrational frequency calculation were performed at the B3LYP, B3PW91, and MP2 levels of theory. B3LYP and B3PW91 are two DFT methods,[24−26] and MP2 is the second-order Møller−Plesset perturbation theory.[27] The 6-311+G* basis sets[28] were used for B, Li, Na, and K, and the relativistic effective core potential with the LANL2DZ basis set was chosen for Rb ($Z = 37$) and Cs ($Z = 55$).[29,30] Natural bond orbital (NBO)[31−33] analysis and nucleus-independent chemical shift (NICS)[34−36] analysis (Table 4) were carried out at the B3LYP/6-311G*//B3LYP/6-311+G* level and the GIAO B3LYP/6-311G*//B3LYP/6-311+G* level, respectively. The molecular orbital (MO) calculations were performed at the B3LYP/6-311G*//B3LYP/6-311+G* level. All MO diagrams were plotted by using the MOLDEN 3.4 program,[37] and all calculations were completed in the framework of Gaussian 98 program packages.[38]

3. Results and Discussion

The optimized geometry parameters for the planar anionic B_7^- (D_{7h}) ring and pyramidal MB_7 (C_{7v}) species are compared in Table 1. Total energies including the zero-point energies and the numbers of imaginary frequencies for MB_7 (C_{7v}) species are shown in Table 2.

3.1. Structure and Stability of the Pyramidal MB_7 (C_{7v}) Species. It can be seen that the calculated B−B bond length is almost identical in B_7^- and MB_7 (Table 1), and that the M−B bond lengths are longer than the sum of covalent radii of the corresponding metal atom (M) and B atom. The covalent radius of the metal atom is 1.22, 1.57, 2.02, 2.16, and 2.35 Å for Li, Na, K, Rb, and Cs, respectively.[39] The covalent radius of boron is 0.88 Å.[39] NBO analysis shows that the average Wiberg bond index (WBI) of the adjacent B atoms is 1.46 in the MB_7 species, which is similar to that in the D_{7h} symmetric B_7^- ring (1.47), while the WBI of M−B bond is near zero. These results imply that the cationic ions have little effect on the structure of the planar heptagon anionic B_7^- (D_{7h}) cluster, and that there is no direct covalent bonding between the alkali-metal atom (M) and B atom. The NBO analyses show that natural charges of all the alkali metals are positive, and the charges of all the boron atoms

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TABLE 1: Calculated Bond Lengths (Å) and Angles (deg) and the Sum of Covalence Radii (Å) for the B_7^- (D_{7h}) and Pyramidal MB_7 (M = Li, Na, K, Rb, or Cs) Species[a]

species	level	r(M−B)	r(B−B)	∠(BMB)	∠(BBB)	sum of covalence radii for M and B[b]
B_7^- (D_{7h})	B3LYP		1.547		128.57	1.76[c]
	B3PW91		1.549		128.57	
	MP2		1.566		128.57	
LiB_7 (C_{7v})	B3LYP	2.372	1.546	38.0	128.57	2.10
	B3PW91	2.377	1.548	38.0	128.57	
	MP2	2.415	1.565	37.8	128.57	
NaB_7 (C_{7v})	B3LYP	2.783	1.547	32.27	128.57	2.45
	B3PW91	2.786	1.549	32.28	128.57	
	MP2	2.818	1.566	32.27	128.57	
KB_7 (C_{7v})	B3LYP	3.191	1.545	28.0	128.57	2.90
	B3PW91	3.173	1.547	28.2	128.57	
	MP2	3.167	1.565	28.6	128.57	
RbB_7 (C_{7v})	B3LYP	3.470	1.546	25.7	128.57	3.04
	B3PW91	3.448	1.548	25.9	128.57	
	MP2	3.507	1.565	25.8	128.57	
CsB_7 (C_{7v})	B3LYP	3.704	1.546	24.1	128.57	3.23
	B3PW91	3.672	1.548	24.3	128.57	
	MP2	3.735	1.565	24.2	128.57	

[a] The 6-311+G* basis set was used for B, Li, Na, and K; the LANL2DZ basis set was used for Rb and Cs. [b] Reference 39. [c] The covalence radius of boron is 0.88 Å, ref 39.

TABLE 2: Total Energies (E)[a] and Zero-Point Energies (ZPEs)[b] for MB_7 (C_{7v}) Species (M = Li, Na, K, Rb, or Cs)[c]

	B3LYP		B3PW91		MP2	
species	E[a]	ZPE[b]	E[a]	ZPE[b]	E[a]	ZPE[b]
LiB_7	−181.22077	16.6 (0)	−181.11102	16.5 (0)	−180.52037	16.7 (0)
NaB_7	−335.97789	15.4 (0)	−335.83221	15.2 (0)	−334.90282	16.4 (0)
KB_7	−773.61913	15.0 (0)	−773.46091	14.9 (0)	−772.37500	16.6 (0)
RbB_7	−197.54335	14.6 (0)	−197.46482	14.5 (0)	−196.62988	16.6 (2)
CsB_7	−193.55736	14.3 (0)	−193.48255	14.2 (0)	−192.65500	17.1 (2)

[a] Total energies in hartrees. [b] Zero-point energies in kilocalories per mole. The integers in parentheses are the number of imaginary frequencies (NIMAG). [c] The 6-311+G* basis set was used for B, Li, Na, and K; the LANL2DZ basis set was used for Rb and Cs.

TABLE 3: Zero-Point-Corrected B3LYP Energies (kcal/mol) for Hypothetical $MB_7 \rightarrow M^+ + B_7^-$ Reactions (M = Li, Na, K, Rb, or Cs)[a]

	LiB_7	NaB_7	KB_7	RbB_7	CsB_7
$MB_7 \rightarrow M^+ + B_7^-$ (D_{7h})[b]	163.3	136.0	116.1	103.6	96.5
$MB_7 \rightarrow M^+ + B_7^-$ (C_{2v})[c]	86.5	59.1	39.3	26.8	19.8

[a] The 6-311+G* basis set was used for B, Li, Na, and K; the LANL2DZ basis set was used for Rb and Cs. [b] The anionic B_7^- (D_{7h}) is the perfect planar structure with D_{7h} symmetry. [c] The global minimum anionic B_7^- is a quasi-planar hexagonal pyramidal structure with C_{2v} symmetry.

TABLE 4: Harmonic Frequencies (cm^{-1}) and Their IR Intensities (km mol^{-1}) in Parentheses for the MB_7 Species (M = Li, Na, and K), at the B3LYP/6-311+G* and MP2/6-311+G* Levels

ω	LiB_7, B3LYP	LiB_7, MP2	NaB_7, B3LYP	NaB_7, MP2	KB_7, B3LYP	KB_7, MP2
ω_1	373 (0)	359 (0)	173 (0)	179 (2)	142 (0)	151 (2)
ω_2	188 (0)	185 (0)	169 (0)	182 (0)	154 (0)	168 (0)
ω_3	406 (10)	402 (14)	240 (18)	238 (21)	187 (1)	196 (18)
ω_4	288 (0)	292 (0)	250 (0)	246 (0)	225 (0)	202 (0)
ω_5	352 (0)	387 (0)	301 (0)	607 (0)	284 (0)	769 (0)
ω_6	398 (0)	399 (0)	382 (0)	379 (0)	366 (0)	356 (0)
ω_7	744 (1)	723 (1)	739 (0)	718 (0)	739 (0)	717 (0)
ω_8	913 (35)	945 (90)	911 (26)	949 (171)	912 (64)	950 (192)
ω_9	1278 (0)	1244 (0)	1277 (0)	1239 (0)	1279 (0)	1244 (0)
ω_{10}	1428 (0)	1482 (0)	1417 (0)	1492 (0)	1491 (0)	1503 (0)

TABLE 5: Harmonic Frequencies (cm^{-1}) and Their IR Intensities (km mol^{-1}) in Parentheses for RbB_7, CsB_7 (C_{7v}), and B_7^- (D_{7h})[a]

ω	RbB_7, B3LYP	RbB_7, MP2	CsB_7, B3LYP	B_7^-, HF⁻	B_7^-, B3LYP	B_7^-, MP2
ω_1	118 (0)	117 (2)	112 (0)			
ω_2	129 (0)	i363 (0)	109 (0)		1221i (0)	452i (0)
ω_3	140 (15)	133 (16)	121 (14)	180 (0)		
ω_4	206 (0)	335 (0)	196 (0)	252 (0)	159 (0)	139 (0)
ω_5	251 (0)	949 (224)	211 (0)	319 (0)	170 (0)	335
ω_6	358 (0)	159 (0)	350 (0)	504 (0)	340 (0)	713
ω_7	738 (0)	716 (0)	738 (0)	767 (0)	735 (0)	1159
ω_8	910 (17)	1027 (0)	910 (16)	926 (196)	907 (8)	945 (352)
ω_9	1276 (0)	1292 (0)	1276 (0)	1334 (0)	1271 (0)	1235
ω_{10}	1415 (0)	1500 (0)	1415 (0)	1426 (0)	1409 (0)	1495

[a] The 6-311+G* basis set was used for B; the LANL2DZ basis set was used for Rb and Cs.

are negative. Therefore, it can be concluded that the electrostatic interaction is dominant in these clusters. The change trend of WBI for metal−boron bonds is that the lighter the metal, the greater the M^+ effects on the planar heptagon B_7^- ring. From the viewpoint of atomic charge, it seems that the MB_7 species (C_{7v}) is a complex of cationic ion M^+ and planar heptagon anion B_7^- (D_{7h}).

The average B−B bond length of the MB_7 species is 1.546 Å (B3LYP), 1.548 Å (B3PW91), and 1.566 Å (MP2), which is shorter than the single B−B bond length of 1.59 Å[40] in B_2. The WBI of the B−B bond, 1.46, in the MB_7 species indicates that the B−B bond is strong between the standard single and the standard double bonds, and the bonding electrons among the B−B bonds are highly delocalized in the planar heptagonal ring. On one hand, there exists torsion action between the B−B σ bonds in the planar B_7^- ring; on the other hand, the multicentered bonds and the delocalized bonds try to compensate for the electron deficiency and thus contribute to the special stablility of the planar B_7^- ring. It is reasonable to assume that a pyramidal MB_7 (C_{7v}) structure could exist.

It is seen that the MB_7 (M = Li, Na, K, Rb, Cs) (C_{7v}) clusters are minima on the potential surfaces at all methods except for RbB_7 (C_{7v}) and CsB_7 (C_{7v}) species at the MP2 level (Table 2). Table 3 gives the energy change in the reaction MB_7 (C_{7v}) → $M^+ + B_7^-$ (D_{7h} or C_{2v}) at the B3LYP/6-311+G* level. In this reaction, the B_7^- cluster was assumed to be either the planar D_{7h} symmetric structure or the pseudoplanar hexagon-capped C_{2v} symmetric structure (at the global minimum on the potential surface). The energy change shows that all the MB_7 species lie below the sum of energies of M^+ and B_7^-; therefore, the reaction is endothermic. Furthermore, the lighter the metal, the higher the dissociation energy. The energy change of the reaction also shows that the D_{7h} symmetric B_7^- structure is unstable compared with the C_{2v} symmetric structure in the $^1A_1$ state.

The calculated harmonic vibrational frequencies and their intensities are listed in Tables 4 and 5. It can be seen that the planar heptagonal B_7^- ring (D_{7h}) structure is a local minimum at the HF/6-311+G* level (Table 5); however, it is the second-order saddle point on the potential energy surface at the B3LYP and MP2 levels. Following the direction of the imaginary vibrational modes, we obtained a bent C_s symmetric structure, which is a local minimum at the B3LYP level or a transition state at the MP2 level. At the HF level, the C_s symmetric structure is also a local minimum. The pseudoplanar hexagon-capped structure of B_7^- (C_{2v}, $^1A_1$) is found to be the global minimum at all methods. But, it could be expected that the planar heptagonal B_7^- ring with D_{7h} symmetry may be stabilized by combining with a cation, M^+ (M = Li, Na, K, Rb, or Cs), forming the MB_7 (C_{7v}) species. Except for the three doubly imaginary frequencies in Table 5, the rest of the lowest frequencies are large enough, which proves that MB_7 is a

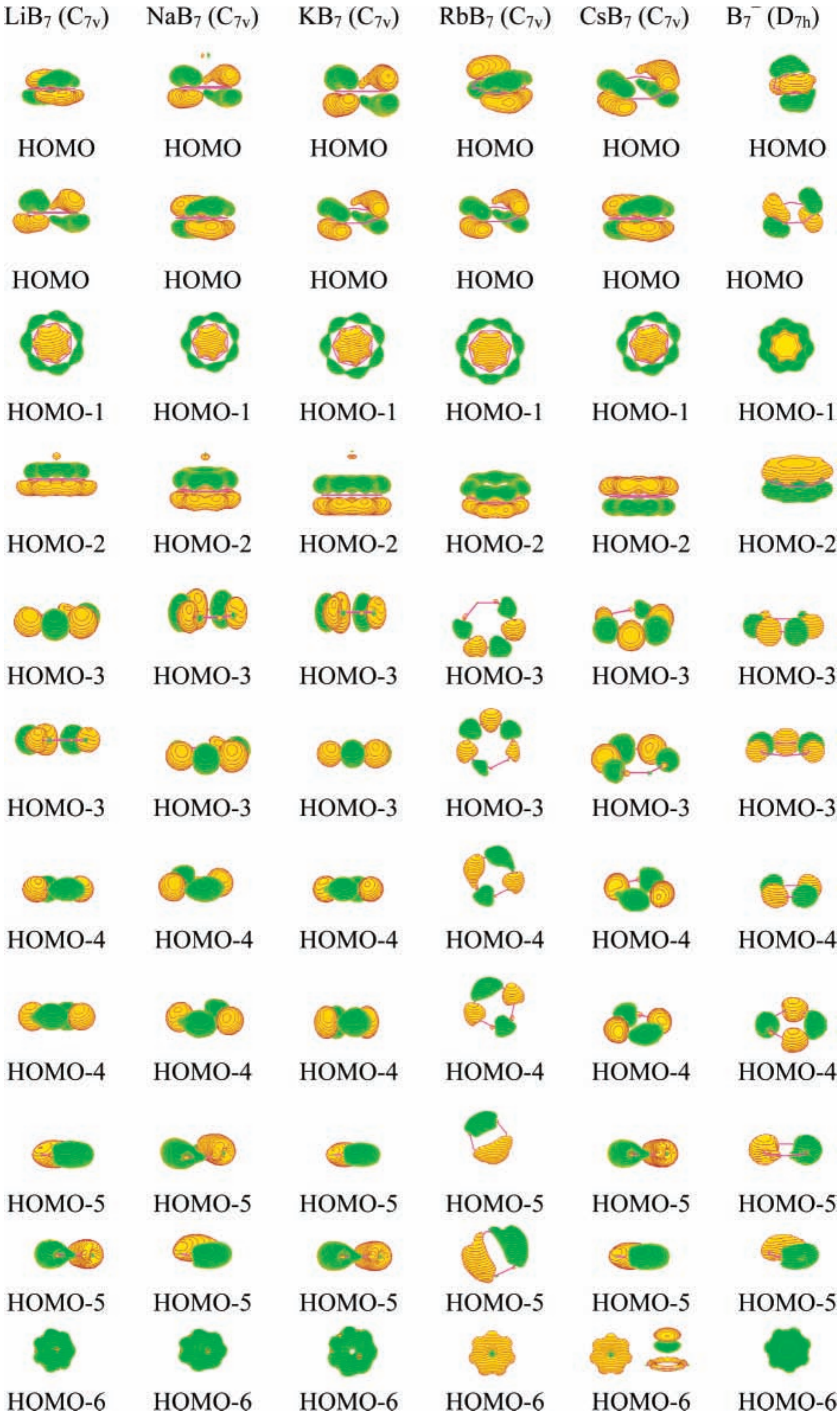

Figure 1. Molecular orbitals of pyramidal MB_7 (C_{7v}) (M = Li, Na, K, Rb, or Cs) and bare B_7^- (D_{7h}) from the HOMO down to the sixth valence molecular orbital (HOMO − 6).

genuine minimum. The vibrational mode corresponds to the metal−ring deformation (except for the RbB_7 and CsB_7 species at the MP2/6-311+G* level), and hardly affects the ring structure as such. The most intensive frequency corresponds to the in-plane deformation of the heptagonal ring in these MB_7 species, which is a candidate for spectroscopic identification. Moreover, the calculated frequencies of the bare planar B_7^- ring are identifiable in the MB_7 (C_{7v}) species (Tables 4 and 5).

3.2. Aromaticity of the MB_7 (C_{7v}) (M = Li, Na, K, Rb, or Cs) Species. The MOs of MB_7 (M = Li, Na, K, Rb, Cs) (C_{7v}) and B_7^- (D_{7h}) are similar to each other, which are shown in Figure 1. The doubly degenerate HOMOs are two π-bonding orbitals, which are mainly composed of the out-of-plane 2p orbitals. HOMO − 2 is also a π-bonding orbital, mainly formed from the out-of-plane 2p orbitals of all B atoms. HOMO − 1 and HOMO − 6 are two multicentered centripetal σ orbitals, which are comprised mainly of the 2p and 2s orbital in-ring plane. All together, there are three π-bonding MOs and two multicenter σ MOs. It is the π MOs that give the agreement with the famous ($4n + 2$) Hückel rule and render the pyramidal

TABLE 6: NICS Values for MB_7 and B_7^- Species[a]

	LiB_7	NaB_7	KB_7	RbB_7	CsB_7	B_7^- (C_{2v})	B_7^- (D_{7h})
NICS(0.0)	−44.23	−41.08	−40.87	−39.36	−39.38	+1.57	−49.92

[a] The NICS (ppm) is calculated at the GIAO B3LYP/6-311G* level of theory on the B3LYP geometry. Each ghost atom is placed on the geometric centers. During the optimization of geometries, the 6-311+G* basis set is used for B, Li, Na, and K, and the LANL2DZ basis set is used for Rb and Cs.

MB_7 species aromatic. The two multicenter σ MOs also render the cluster σ aromatic.

Generally, there are energetic (resonance and aromatic stabilization (ASE) energies),[36,41] magnetic (^{1}H NMR chemical shifts, magnetic susceptibility anisotropies and their exaltations, and NICS),[2,35] and geometric (bond length equalization)[42,43] criteria for aromaticity. The NICS, which was proposed by Schleyer and co-workers, is an easy and efficient criterion to identify two- and three-dimensional aromatic nature. Aromaticity is characterized by a negative NICS value, antiaromaticity by a positive NICS, and nonaromaticity by an NICS close to zero.

As listed in Table 6, the NICS (0.0) at the center of the C_{7v} symmetric MB_7 (M = Li, Na, K, Rb, or Cs) structure was calculated to be −44.23, −41.08, −40.87, −39.36, and −39.38 ppm, respectively, indicating all the MB_7 species are very aromatic. For the planar anionic B_7^- (D_{7h} symmetry), the NICS values at the ring center (NICS(0.0)) or 0.5 or 1.0 Å below (NICS(0.5) or NICS(1.0)) were computed to be −49.92, −40.42, and −23.99 ppm, respectively, at the GIAO B3LYP/6-311G*//B3LYP/6-311+G* level. This shows that the anionic planar B_7^- (D_{7h} symmetry) is also very aromatic. The NICS (1.0) value was selected as a criterion to minimize the local contributions in the small-ring cluster.[44] However, for the global minimum pseudoplanar B_7^- with C_{2v} symmetry in its $^1A_1$ ground state, the NICS(0.0), NICS(0.5), and NICS(1.0) were calculated to be +1.57, +6.177, and +10.20 ppm, respectively, indicating antiaromaticity. So, it can be concluded that the alkali-metal cation M^+ affects the planar B_7^- ring (D_{7h}) to a very low degree, but influences the global minimum pseudoplanar B_7^- (C_{2v}) in the $^1A_1$ state greatly. This proves that the pyramidal MB_7 (M = Li, Na, K, Rb, or Cs) species with C_{7v} symmetry are stable.

4. Summary

The alkali-metal−B_7 pyramidal MB_7 (M = Li, Na, K, Rb, or Cs) (C_{7v}) clusters were investigated theoretically. These compounds are genuine minima except RbB_7 and CsB_7 at the MP2 level. From the ion point of the view, they may be taken as a combination between M^+ and a planar heptagonal anionic B_7^- ring. The thermochemistry analysis, namely, energy change in dissociation, shows that the MB_7 species may be observed in a future experiment. And the NBO, NICS, and molecular orbital analyses show that there are two multicenter σ bonds and three occupied delocalized π bonds in the electronic structures. This conforms to the $(4n + 2)$ aromaticity counting rule, indicating the planar heptagonal B_7^- ring in the pyramidal MB_7 (C_{7v}) species is very aromatic.

References and Notes

(1) Van Zandwijk, G.; Janssen, R. A. J.; Buck, H. M. *J. Am. Chem. Soc.* **1990**, *112*, 4155.

(2) Schleyer, P. v. R.; Jiao, H.; Hommes, N. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.

(3) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity*; Wiley: New York, 1994.

(4) Goldfuss, B.; Schleyer, P. v. R. *Organometallics* **1997**, *16*, 1543.

(5) Li, X. W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578.

(6) Li, X. W.; Xie, Y.; Schreiner, P. R.; Gripper, K. D.; Crittendon, R. C.; Campana, C. F.; Schaeter, H. F.; Robinson, G. H. *Organometallics* **1996**, *15*, 3797.

(7) Robinson, G. H. *Acc. Chem. Res.* **1999**, *32*, 773.

(8) Li, X.; Kuznetsov, A. E.; Zhang, H. F.; Boldyrev, A. I.; Wang, L. S. *Science* **2001**, *291*, 859.

(9) Kuznetsov, A. E.; Boldyrev, A. I.; Li, X.; Wang, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 8825.

(10) Li, X.; Zhang, H. F.; Wang, L. S.; Kuznetsov, A. E.; Cannon, N. A.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 1867.

(11) Kuznetsov, A. E.; Boldyrev, A. I. *Struct. Chem.* **2002**, *13*, 141.

(12) Kuznetsov, A. E.; Corbett, J. D.; Wang, L. S.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 3369.

(13) Alexandrova, A. N.; Boldyrev, A. I. *J. Phys. Chem. A* **2003**, *107*, 554.

(14) Alexandrova, A. N.; Boldyrev, A. I., Zhai, H. J.; Wang, L. S.; Steiner, E.; Fowler P. W. *J. Phys. Chem. A* **2003**, *107*, 1359.

(15) Zhai, H. J.; Wang, L. S.; Alexandrova, A. N.; Boldyrev, A. I., Steiner, E.; Fowler, P. W. *J. Chem. Phys.* **2002**, *117*, 7917.

(16) Ma, J.; Li, Z. H.; Fan, K. N.; Zhou, M. F. *Chem. Phys. Lett.* **2003**, *372*, 708.

(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) Li, Q. S.; Jin Q. *J. Int. Quantum Chem.* **2003**, *94*, 269.

(20) Burdett, J. K.; Canadell, E.; Miller, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 6561.

(21) Burdett, J. K.; Canadell, E. *Inorg. Chem.* **1988**, *27*, 4437.

(22) Thomas, P. F. *J. Solid State Chem.* **2000**, *154*, 110.

(23) Li, Q. S.; Jin, Q. *J. Phys. Chem. A* **2003**, *107*, 7874.

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

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

(26) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(27) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(28) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbial Theory*; Wiley: New York, 1986.

(29) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

(30) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(31) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct.: THEOCHEM* **1988**, *169*, 41.

(32) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(33) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(34) Schleyer, P. v. R.; Maerker, C.; Dransfekd, A.; Jiao, H.; Hommes, N. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(35) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209.

(36) Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *Organometallics* **1996**, *15*, 1755.

(37) Schaftenaar, G. *MOLDEN 3.7*; CAOS/CAMM Center: The Netherlands, 1998.

(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; 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.

(39) *Periodic Table of Elements*; Wiley-VCH: Weinheim, Germany, 1997.

(40) Huber K. P.; Herzberg G. *Molecular Spectra and molecular Structure, Vol. 4. Constants of Diatomic molecules*; Van Nostrand Reinhold: New York, 1979.

(41) Glukhovtsev, M. *J. Chem. Educ.* **1997**, *74*, 132.

(42) Eluvathingal, D. J.; Boggavarapu, K. *Inorg. Chem.* **1998**, *37*, 2110.

(43) Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70.

(44) Schleyer, P. v. R.; Manoharan, M.; Wang, Z. X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465.