Inorg. Chem. **2008**, *47*, 2098−2102

Inorganic Chemistry
Article

Stabilization of an All-Metal Antiaromatic Molecule (Al_4Li_4) Using BH and C as Caps

Priyadarshi Satpati* and K. L. Sebastian

Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 560012, India

Received May 29, 2007

It has been reported by Pati et al. (*J. Am. Chem. Soc.* **2005**, *127*, 3496) that coordination with a transition metal can stabilize the “antiaromatic”, all-metal compound Al_4Li_4. Here, we report that it can also be stabilized by capping with a main group element like C and its isoelectronic species BH. Our calculations of binding energy, nuclear independent chemical shift, energy decomposition analysis, and molecular orbital analysis support the capping-induced stability, reduction of bond length alternation, and increase of aromaticity of these BH/C-capped Al_4Li_4 systems. The interaction between p_x and p_y orbitals of BH/C and the HOMO and LUMO of Al_4Li_4 is responsible for the stabilization. Our calculations suggest that capping can introduce fluxionality at room temperature.

1. Introduction

The concepts of aromaticity and antiaromaticity are of fundamental interest in chemistry.[1–4] The concepts have recently been extended to all metal compounds.[5–9] Gas-phase observations of MAl_4^- (M = Li, Na, and Cu) and $Li_3Al_4^-$ coupled with computations led to the conclusion that Al_4^{2-}[5,10] is “aromatic”, while Al_4^{4-} has been claimed to be “antiaromatic”.[11] However, Schleyer et al. have argued that Al_4^{4-} is more σ-aromatic than π-antiaromatic.[12] Havenith et al.[13] studied the ring current patterns of Al_4Li_4 and concluded that, although the $(4n + 2)$ π-electron count suggests aromaticity and hence diatropicity, the π orbital is magnetically inactive in Al_4^{2-}. However, the paratropic ring current supports the antiaromatic nature of $Li_3Al_4^-$ and Li_4Al_4. Thus, they showed that simple electron-counting is insufficient to conclude whether a system is aromatic or antiaromatic. Until now, these clusters have been synthesized only in the gas phase by a laser vaporization technique, which is insufficient for providing structural details. It would be of great interest if we can stabilize Al_4Li_4 by attaching a suitable group. For such systems, the bond-length alternation and charge densities (at the ring critical point), which are well established parameters for characterizing aromaticity, can be measured and calculated. Datta and Pati[14] showed that Al_4M_4 (M =

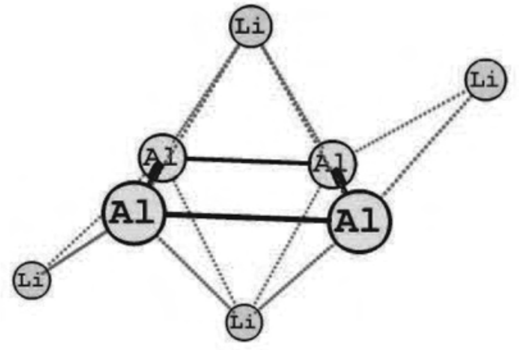

Figure 1. Free Al_4Li_4 (C_{2h}).

---

* Author to whom correspondence should be addressed. E-mail: psatpati@ipc.iisc.ernet.in.

(1) Minkin, V. I.; Glukhontsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity*; Wiley: New York, 1974.
(2) Shaik, S.; Shurki, A.; Danovich, D.; Hilberty, P. C. *Chem. Rev.* **2001**, *101*, 1501–1539.
(3) Gomes, J. A. N. F.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1359–1383.
(4) Shetty, S.; Kar, R.; Kanhere, D. G.; Pal, S. *J. Phys. Chem. A* **2006**, *110*, 252–256.
(5) Li, X.; Kuzentsov, A.; Zhang, H.-F.; Boldyrev, A. I.; Wang, L. *Science* **2001**, *291*, 859–861.
(6) Li, X. H.-F.; Wang, L.-S.; Kuznetsov, A. E.; Cannon, N. A.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 1867–1870.
(7) Kuznetsov, A.; Boldyrev, A. I.; Li, X.; Wang, L.-S. *J. Am. Chem. Soc.* **2001**, *123*, 8825–8831.
(8) Datta, A.; Mallajosyula, S. S.; Pati, S. K. *Acc. Chem. Res.* **2007**, *40*, 213–221.
(9) Schleyer, P. v. R. *Chem. Rev.* **2001**, *101*, 1115–1117.
(10) Boldyrev, A. I.; Wang, L. *Chem. Rev.* **2005**, *105*, 3716–3757.
(11) Li, X.; Kuzentsov, A.; Zhang, H.-F.; Boldyrev, A. I.; Wang, L. *Science* **2003**, *300*, 622.
(12) Chen, Z.; Corminboeuf, C.; Heine, T.; Bohmann, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2003**, *125*, 13930.
(13) Havenith, R. W. A.; Fowler, P. W.; Steiner, E.; Shetty, S.; Kanhere, D. G.; Pal, S. *Phys. Chem. Chem. Phys.* **2004**, *6*, 285.

10.1021/ic701040g CCC: $40.75

Table 1. Energy (in au), Bond Lengths and Their Alternations (BLA) and Distances (in Å), and Nuclear Independent Chemical Shift (NICS) (in ppm), Using Two Basis Sets[a]

molecule (symmetry)	method	energy	long Al−Al distance	short Al−Al distance	bond length alternation	NICS at the center of the Al_4Li_4 ring
Al_4 Li_4 (C_{2h})	6-311++G**	−999.9330848	2.68	2.55	0.13	−11.407
Al_4 Li_4 (C_{2h})	LANL2DZ	−38.0803442	2.77	2.64	0.13	−9.313

[a] The results, though with better basis sets, are in close agreement with those of Boldyrev et al.[11] and Pati et al.[18]

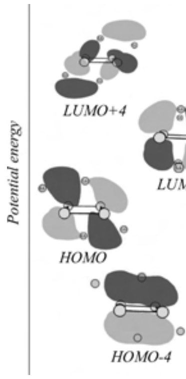

Figure 2. HOMO-4, HOMO, LUMO, and LUMO+4 are the four π-molecular orbitals of Al_4Li_4. The LUMO is rotated by 90° for clarity.

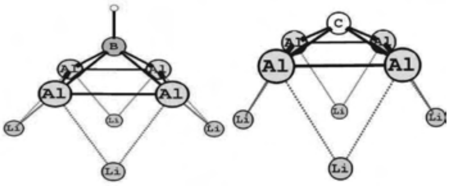

Figure 3. C_{2v} geometry of η^4-Al_4Li_4-BH and η^4-Al_4Li_4-C.

Li, Na, and K) are very good candidates for higher-order nonlinear optical applications due to charge transfer from the highly electropositive ions (Li, Na, and K) to the Al_4 ring.

The synthesis of an antiaromatic compound is difficult because of its instability. Cyclobutadiene (C_4H_4), a 4π-electron system, remained unisolated for a long time. Longuet-Higgins and Orgel proposed, in a landmark paper,[15,16] that there will be stable complexes involving it and transition metals.[17] Following this idea, Dutta and Pati[18] suggested stable complexes of Al_4Li_4 species with $Fe(CO)_3$. A sandwich compound of Al_4Li_4 with Ni was also proposed. They concluded that complexation with 3d transition metal ions stabilizes the frontier orbital and introduces aromatic character by adding two electrons in the lowest unoccupied molecular orbital (LUMO) of Al_4Li_4.

In this paper, we propose a few compounds of Al_4Li_4 by capping with a main group element like C and its isoelectronic species BH. The CH^+ species is an isolobal analogue of $Fe(CO)_3$, which is well-known for stabilizing C_4H_4. We found that capping with CH^+ stabilizes Al_4Li_4, but to avoid extra charge, we explore capping with C and its isoelectronic species BH. The parent compound $Li_3Al_4^-$ itself is known only as an ion in the vapor phase. So the synthesis would be a challenge. Perhaps one possibility would be to take a fused mixture/alloy containing Li−Al−C and vaporize it using a laser pulse. A wide range of anionic clusters may be produced, from which the desired cluster [$Al_4Li_3C^-$] may be selected using a mass gate and consequently studied by photoelectron spectroscopy. An alternative could be to use the alloy as one of the electrodes in an electric discharge. The same could be done with Li−Al−B in the presence of H_2 gas. The reported compounds show high binding energy and high aromatic character. Our calculations show that d orbitals on the capped atom are not necessary to stabilize the antiaromatic Al_4Li_4. A suitable size, shape, and energy of the p orbitals of the capping species are sufficient to cause stability. We performed *ab initio* calculations on Al_4Li_4BH and Al_4Li_4C using Gaussian 03[19] software. The calculation uses a density functional method with the B3LYP[20,21] exchange correlation functional. We have used two different basis sets (6-311++G** and LANL2DZ) to check the consistency of the results.

C_4H_4 is antiaromatic according to Hückel π -electron theory. Distortion to the rectangular geometry lifts the orbital degeneracy and leads to a singlet ground state. Distorted square-planar geometry is the transition state for fluxional rearrangement, where one rectangular form is converted to the other. In Al_4Li_4, the electropositive Li atoms donate electrons to the Al_4 ring, and as a result, it forms Al_4^{4-} with 4π electrons, similar to the situation in C_4H_4. In the case of Al_4Li_4, $\sigma-\pi$ separation is poor because of the small energy gap between σ and π molecular orbitals. So any consideration of aromaticity has to incorporate both σ and π electrons. In Al_4^{4-}, the σ electrons try to equalize all the bonds between Al atoms, while the π electrons would cause bond length alternation (BLA). BLA may be measured by the average difference between the bond lengths of two consecutive bonds in the four-membered ring. Our idea is to minimize the distortive effect of π electrons by introducing two more electrons to the π-type LUMO of Al_4Li_4.

The ground-state structure for the singlet state of Al_4Li_4 is found to be a rectangular Al_4 geometry (similar to C_4H_4) with surrounding Li atoms. The closed-shell C_{2h} geometry is reported to be the most stable isomer.[18] We optimize the C_{2h} geometry shown in Figure 1, and the optimized parameters using 6-311++G** and Lanl2dz basis sets are given in Table 1. Structural parameters are in very good agreement with the earlier report which used the 6-311+G* basis set.[11]

---

(14) Datta, A; Pati, S. K. *J. Phys. Chem. A* **2004**, *108*, 9527.
(15) Longuet-Higgins, H. C.; Orgel, L. E. J. *J. Chem. Soc.* **1956**, 1969–1972.
(16) Collmann, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; Oxford University Press: Oxford, U.K., 1987.
(17) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988.
(18) Datta, A.; Pati, S. K. *J. Am. Chem. Soc.* **2005**, *127*, 3496–3500.
(19) Frisch, M. J. *Gaussian 03*, revision B.03; Gaussian Inc.: Pittsburg, PA, 2003.
(20) Lee, C.; Yang, W.; Parr, R. G. *J. Chem. Phys.* **1993**, *98*, 5648.
(21) Becke, A. D. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785.

Table 2. Single-Point Energy Decomposition Analysis, Energy in kcal/mol for the Compounds η^4-Al_4Li_4-BH and η^4-Al_4Li_4-C

energy components	η^4-Al_4Li_4-BH			η^4-Al_4Li_4-C		
	C_{4v}	C_{2v}	energy diff. ($E_{C_{2v}} - E_{C_{4v}}$)	C_{4v}	C_{2v}	energy diff. ($E_{C_{2v}} - E_{C_{4v}}$)
electrostatic kinetic	−609.83	−612.02	−2.19	−629.09	−627.70	+1.39
energy	507.96	504.77	−3.19	486.58	486.09	−0.49
coulomb (steric + orbit)	215.42	218.73	+3.31	253.27	250.51	−2.76
XC energy	693.91	693.06	+0.85	650.82	650.72	+0.1
total energy	−580.36	−581.59	−1.22	−540.07	−541.82	−1.76

Table 3. Binding Energy and Energy Difference (in kcal/mol), Nuclear Independent Chemical Shift (NICS) (in ppm), and Bond Length Alternation (BLA) (in Å) for the Two Compounds

molecule (symmetry)	method	binding energy	NICS at the center of the Al_4Li_4 ring	bond length alternation	energy barrier for fluxionality energy diff. ($E_{C_{4v}} - E_{C_{2v}}$)
η^4-Al_4Li_4-BH (C_{2v})	6-311++G**	109.549	−49.347	0.05	0.928149
	LANL2DZ	112.969	−46.289	0.05	1.05453
η^4-Al_4Li_4-C (C_{2v})	6-311++G**	194.405	−58.564	0.03	1.71649
	LANL2DZ	184.478	−50.429	0.04	2.52215

Table 4. Energies of HOMO and LUMO of Free Al_4Li_4 and the Molecular Orbitals That Result from Their Interaction with the p_x and p_y Orbitals of the Caps BH and C[a]

molecule (symmetry)	6-311++G**			LANL2DZ		
	HOMO	LUMO	(LUMO−HOMO)	HOMO	LUMO	(LUMO−HOMO)
Al_4Li_4 (C_{2h})	−0.1290	−0.0760	0.053	−0.1324	−0.0802	0.0522
	HOMO-2	HOMO-1	(HOMO-1−HOMO-2)	HOMO-2	HOMO-1	(HOMO-1−HOMO-2)
η^4-Al_4Li_4-BH (C_{2v})	−0.1629	−0.1590	0.0039	−0.1655	−0.1621	0.0034
	HOMO-3	HOMO-2	(HOMO-2-HOMO-3)	HOMO-3	HOMO-2	(HOMO-2-HOMO-3)
η^4-Al_4Li_4-C (C_{2v})	−0.1964	−0.1911	0.0053	−0.1964	−0.1912	0.0052

[a] Energies are given in atomic units.

The bond length alternation of 0.13 Å suggests Al_4Li_4 to be an antiaromatic compound. But the negative magnitude of nuclear independent chemical shift (NICS, at the center of the ring), −11.407 ppm (using the 6-311++g** basis set) and −9.313 ppm (using the LANL2DZ basis set) of Al_4Li_4, supports the claim by Schleyer et al.[12] that Al_4Li_4 has higher σ aromaticity than π antiaromaticity.[22] There are four π molecular orbitals of Al_4Li_4 (see Figure 2). Among these four π molecular orbitals, two are filled up with the four available electrons, and this is responsible for the antiaromaticity of Al_4Li_4. The doubly occupied HOMO is responsible for the rectangular shape of the Al_4 ring. If one introduces two more electrons so that the LUMO of Al_4Li_4 also gets filled, one can expect bond length equalization. To achieve this, we assume Al_4Li_4 to be coordinated with C/BH. We find that the resultant compounds are stable and the binding increases the aromatic character and reduces the bond length alternation. We conclude that Al_4Li_4 can be stabilized by nontransition metal species too. The stabilization is due to the interaction of p_x and p_y orbitals of C/BH with the ring. We also find that the capping reduces the activation barrier for fluxional rearrangement and causes fluxionality at room temperature.

2. η^4-Al_4Li_4-BH and η^4-Al_4Li_4-C

η^4-C_4H_4-$Fe(CO)_3$ was reported long ago.[23] We imagined a new complex by substituting C_4H_4 with Al_4Li_4 and $Fe(CO)_3$ with BH/C. We found that the C_{4v} geometry is not a minimum in the potential energy surface (it shows a single negative frequency of −67 cm^{-1} for η^4-Al_4Li_4-BH and −92 cm^{-1} for η^4-Al_4Li_4-C for the 6-311++g** basis set), whereas the C_{2v} geometry of η^4-Al_4Li_4-BH and η^4-Al_4Li_4-C are true minima with very small bond length alternation. The imaginary frequency associated with the C_{4v} geometry shows predominantly the movement of Li atoms distorting to give C_{2v} geometry. To understand why the C_{4v} geometry is not stable, we did a single-point energy decomposition analysis for the optimized structures (C_{4v} and C_{2v}) of η^4-Al_4Li_4-BH and η^4-Al_4Li_4-C using the TZ2P basis set and ADF package.[24,25] The results are given in Table 2. Energy decomposition analysis clearly suggests that the driving force for the change in geometry (from C_{4v} to C_{2v}) is mainly due to the reduction of kinetic energy along with electrostatic stabilization in the case of η^4-Al_4Li_4-BH and the reduction of Coulombic repulsion in the case of η^4-Al_4Li_4-C. The C_{2v} geometries of η^4-Al_4Li_4-BH and η^4-Al_4Li_4-C are shown in Figure 3. The optimized parameters of interest for these compounds are given in Table 3.

The binding energy or the stability of these compounds can be studied using the following fragmentation scheme:

$$\eta^4\text{-}Al_4Li_4\text{-}BH = Al_4Li_4 + BH$$

$$\eta^4\text{-}Al_4Li_4\text{-}C = Al_4Li_4 + C$$

The energy of singlet Al_4Li_4 (C_{2h} symmetry) has been used to calculate the binding energy. The binding energy for η^4-Al_4Li_4-BH is found to be 109.55 kcal/mol (6-311++g**) and 112.97 kcal/mol (LANL2DZ). The binding energy for η^4-Al_4Li_4-C is found to be 194.41 kcal/mol (6-311++g**) and 184.48 kcal/mol (LANL2DZ). In comparison, the reported[18] binding energy of η^4-Al_4Li_4-$Fe(CO)_3$ is 106.04

---

(22) Shetty, S.; Kanhare, D. G.; Pal, S. J. *Phys. Chem. A* **2004**, *108*, 628.

(23) Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131–133.

(24) Bickelhaupt, F. M.; Baerends, E. J. *Rev. Comput. Chem.* **2000**, *15*, 1.

(25) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; van Gibergen, S. J. A.; Fonseca Guerra, C.; Srijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

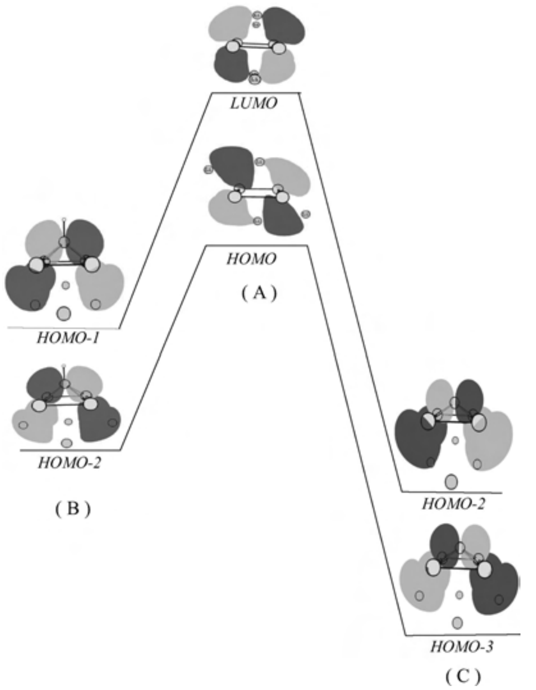

Figure 4. (A) HOMO and LUMO of free Al$_4$Li$_4$. (B) Resultant molecular orbitals formed by the interaction of the HOMO−LUMO of free Al$_4$Li$_4$ and p_x and p_y of the BH cap. (C) Resultant molecular orbitals formed by the interaction of free Al$_4$Li$_4$ and p_x and p_y of the C cap. LUMO of (A), HOMO-1 of (B), and HOMO-2 of (C) are rotated by 90° for clarity.

kcal/mol. The high binding energies for η^4-Al$_4$Li$_4$-BH and η^4-Al$_4$Li$_4$-C suggest that Al$_4$Li$_4$ is very well stabilized with capping by BH or C.

The NICS value at the center of the Al$_4$ ring of the compound η^4-Al$_4$Li$_4$-BH is −49.347 ppm (6-311++g**) and −46.289 ppm (LANL2DZ), whereas for η^4-Al$_4$Li$_4$-C, the NICS value is −58.564 ppm (6-311++g**) and −50.429 ppm (LANL2DZ). The large negative value of NICS suggests more aromatic character in the above compounds than with a reported value of −25.44 ppm for η^4-Al$_4$Li$_4$-Fe(CO)$_3$.[18] The BLA for η^4-Al$_4$Li$_4$-BH is 0.05 Å. η^4-Al$_4$Li$_4$-C shows a BLA of 0.03 Å (for the 6-311++G** basis set) and 0.04 Å (for the LANL2DZ basis set). The bond length alternation of free Al$_4$Li$_4$ is 0.13 Å. The reduction of BLA upon capping with BH or C supports the increase of aromatic character in the Al$_4$ ring. The nonbonding HOMO and LUMO of Al$_4$$^{-4}$ is stabilized by the interaction with the p_x and p_y orbitals of the cap M(BH/C). (The Al$_4$ ring is taken to be in the *xy* plane, with *x* and *y* passing through the center of Al−Al bonds.) The size, energy, and symmetry of p_x and p_y orbitals of carbon are such that the overlap with the HOMO and LUMO of Al$_4$$^{-4}$ is at a maximum, and the result is a higher binding energy of η^4-Al$_4$Li$_4$-C. η^4-Al$_4$Li$_4$-BH is also stable, but the p_x and p_y orbitals of BH are slightly more diffuse than those of carbon. We have identified the two filled molecular orbitals of η^4-Al$_4$Li$_4$-BH and η^4-Al$_4$Li$_4$-C that result from the interaction of p_x and p_y of the cap with the HOMO and LUMO of Al$_4$ Li$_4$. Our calculation shows that, after interacting with the cap, the HOMO and LUMO of free η^4-Al$_4$Li$_4$ are stabilized and change to HOMO-1 and HOMO-2 for η^4-Al$_4$Li$_4$-BH and HOMO-2 and HOMO-3 for η^4-Al$_4$Li$_4$-C, respectively. These molecular orbitals are shown in Figure 4.

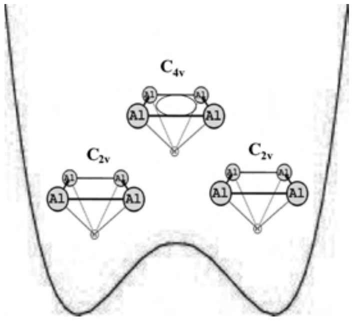

Figure 5. Schematic diagram of fluxionality (M = BH, C).

Table 4 gives the quantitative measure of the stabilization of the HOMO and LUMO of free Al$_4$Li$_4$ upon interaction with the p_x and p_y orbitals of the cap atoms (BH/C). We found that the energy difference between HOMO-2 and HOMO-3 for η^4-Al$_4$Li$_4$-C is larger than the energy difference between HOMO-1 and HOMO-2 of η^4-Al$_4$Li$_4$-BH (see Table 4). A lower energy gap between these two molecular orbitals should imply lower bond length alternation. But the lower bond length alternation and higher negative NICS value (see Table 3) for η^4-Al$_4$Li$_4$-C could be due to the larger effect of σ electrons. Carbon interacts more strongly with the σ molecular orbitals of Al$_4$Li$_4$ than BH due to the suitable size and energy of the p_x and p_y orbitals. Hence, the σ valence molecular orbitals of η^4-Al$_4$Li$_4$-C are more stabilized than those of η^4-Al$_4$Li$_4$-BH.

We investigated the fluxionality of the Al$_4$Li$_4$ ring when it is bonded to the cap of BH and C. When the BLA is less, the energy barrier for ring fluxionality becomes less and the possibility of showing fluxional behavior at room temperature increases. The C_{4v} geometries of η^4-Al$_4$Li$_4$-BH and η^4-Al$_4$Li$_4$-C are identified to be the transition state of fluxional rearrangement (Figure 5). The energy difference between the C_{4v} and C_{2v} geometries of η^4-Al$_4$Li$_4$-BH and η^4-Al$_4$Li$_4$-C (activation energy for fluxional rearrangement) is given in Table 3. A very small activation energy (≃0.9–2.5 kcal/mol) suggests that these molecules will show fluxionality at room temperature. The rate constants for fluxional rearrangement for η^4-Al$_4$Li$_4$-C and η^4-Al$_4$Li$_4$-BH calculated using transition state theory[26] are 3×10^{14} s^{-1} and 9.7×10^{14} s^{-1}, respectively, at 298 K. The frequencies required for the calculation were taken from Gaussian calculations (6-311++g** basis set).

Summary and Conclusions

In conclusion, we have demonstrated that all metal species such as Al$_4$Li$_4$ can be stabilized by capping with BH or C. The stabilization is due to suitable ring cap compatibility between the p_x and p_y orbitals of the capped atom and the HOMO and LUMO of Al$_4$Li$_4$. A donation of two electrons to the ring by the cap atoms introduces aromatic character.

---

(26) Nikitin, E. E. *Theory of Elementary Atomic and Molecular Processes in Gases*; Clarendon Press: Oxford, U.K., 1974.

We also conclude that, to stabilize the antiaromatic compound Al_4Li_4, the presence of d electrons of the cap is not a necessary condition. We have shown that Al_4Li_4 with a BH or C cap has very high binding energy, which suggests that these compounds should be considered as very good candidates for synthesis.

We have shown that, after capping with BH and C, the bond length alternation is reduced to a large extent and the activation barrier for the fluxional motion becomes small. A very high rate of fluxional rearrangement at room temperature suggests that η^4-Al_4Li_4-BH and η^4-Al_4Li_4-C will show fluxionality. We hope that our work will provide a motivation for the synthesis of these molecules.

Acknowledgment. Priyadarshi Satpati is thankful to the Council for Scientific and Industrial Research (CSIR), Govt. of India for financial support, and Supercomputer Education and Research Center (SERC), IISc for the computational facility. We thank Prof. E. D. Jemmis and Mr. Biswarup Pathak for helpful discussions and suggestions.

Supporting Information Available: Cartesian coordinates, total energy (in Hartree), number of imaginary frequencies, and lowest frequency (in cm^{-1}) of the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701040G