Metallo-Antiaromatic Al_4Na_4 and $Al_4Na_3^-$ Compounds: A Theoretical Investigation

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Present theoretical investigation reveals that the Al_4 unit in neutral Al_4Na_4 and anion $Al_4Na_3^-$ clusters has $4n$ π electrons and has a rectangular structure with alternate π bonds. Hence, neutral Al_4Na_4 and anion $Al_4Na_3^-$ clusters satisfy the criteria for antiaromaticity and are metallo-antiaromatic compounds.

I. Introduction

It has been understood for many years that among the simple monocyclic systems, compounds with only $(4n + 2)$ π electrons (where n is an integer), such as benzene, follow Hückel's rule and are aromatic.[1] Conjugated ring systems having $4n$ π electrons do not obey Hückel's rule for aromaticity and can be divided into antiaromatic and nonaromatic compounds. The definition of antiaromaticity is somewhat controversial, but the concept has proven to be of great interest due to the unusual behavior exhibited by the antiaromatic compounds such as instability, magnetic properties, and high reactivity.[2] If we restrict ourselves to the conventional definition of antiaromaticity, then it is known that if the system is planar with $4n$ π electrons and is destabilized due to the electron delocalization, it will be antiaromatic, e.g., cyclobutadiene.[3,4] On the other hand, if the system with $4n$ π electrons buckle to become nonplanar, it is known to lose the antiaromaticity and the system would be nonaromatic, e.g., cyclooctatetraene.[5] However, the distinction between antiaromaticity and nonaromaticity is not very clear. The geometry of the system seems to be one criterion to distinguish antiaromatic and nonaromatic compounds. Cyclobutadiene is a well-known example of antiaromatic compounds.[3,4]

Aromaticity and antiaromaticity have been historically important in organic chemistry. However, in recent years, studies have been carried out to show that aromaticity also exists in organometallic compounds and metal clusters.[6,7,8] In a combined experimental and theoretical work, Li et al. have shown aromaticity in all-metal atom clusters, e.g., MAl_4^- and M_2Al_4 (M = Li, Na, and Cu) for the first time.[8a] On this basis, recently it was shown that the Al_4^{4-} species in the Al_4Li_4 cluster satisfies the criteria of antiaromaticity and hence is an all-metal antiaromatic compound.[9,10] Theoretical proposition of this was presented by us in a recent symposium.[9] However, Kuznetsov et al. have experimentally synthesized the first antiaromatic compound, viz., $Al_4Li_3^-$ and theoretically proved that it also has similar characteristics of the Al_4Li_4 cluster in a receent publication.[10] These studies open up a new area in the field of aromaticity and antiaromaticty in metal compounds.

On this background, we propose a theoretical investigation in this paper to understand the structural and bonding properties in neutral Al_4Na_4 and anion $Al_4Na_3^-$ clusters. We show that the Al_4 species in neutral Al_4Na_4 and anion $Al_4Na_3^-$ is similar to the Al_4 species found in Al_4Li_4 and $Al_4Li_3^-$ clusters and are antiaromatic.

TABLE 1: Bond Length of the Optimized Ground State of Al_4Na_4 and $Al_4Na_3^-$ Clusters[a]

	bond length (Å)
Al (1)−Al(2)	2.852 (2.443)
Al(1)−Al(3)	2.680 (2.288)
Na(6)−Na(7)	3.695 (2.566)
Na(7)−Na(5)	3.695 (2.566)
Na(7)−Na(8)	4.695

[a] The bond lengths of the $Al_4Na_3^-$ cluster are given in parentheses.

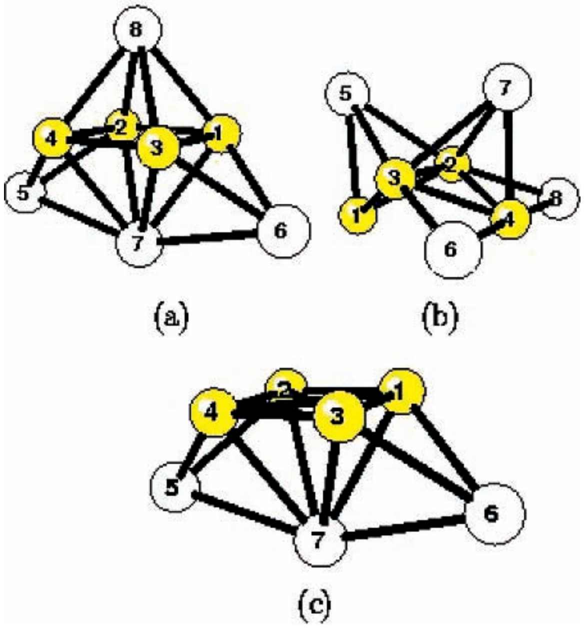

Figure 1. Geometries of Al_4Na_4 and $Al_4Na_3^-$ clusters (at the CCD/6-31G(d,p) level). Spheres 1, 2, 3, and 4 indicate the Al atoms while the rest of the spheres indicate the Na atoms. (a) Ground-state structure of the Al_4Na_4 cluster with a rectangular planar Al_4 unit. (b) Excited-state structure of the Al_4Na_4 cluster with a distorted Al_4 unit. (c) Ground-state structure of $Al_4Na_3^-$ cluster with a rectangular planar Al_4 unit.

Computational Details

We give a brief discussion on the structural property of the Al_4Na_4 cluster since it has been already studied using Born−

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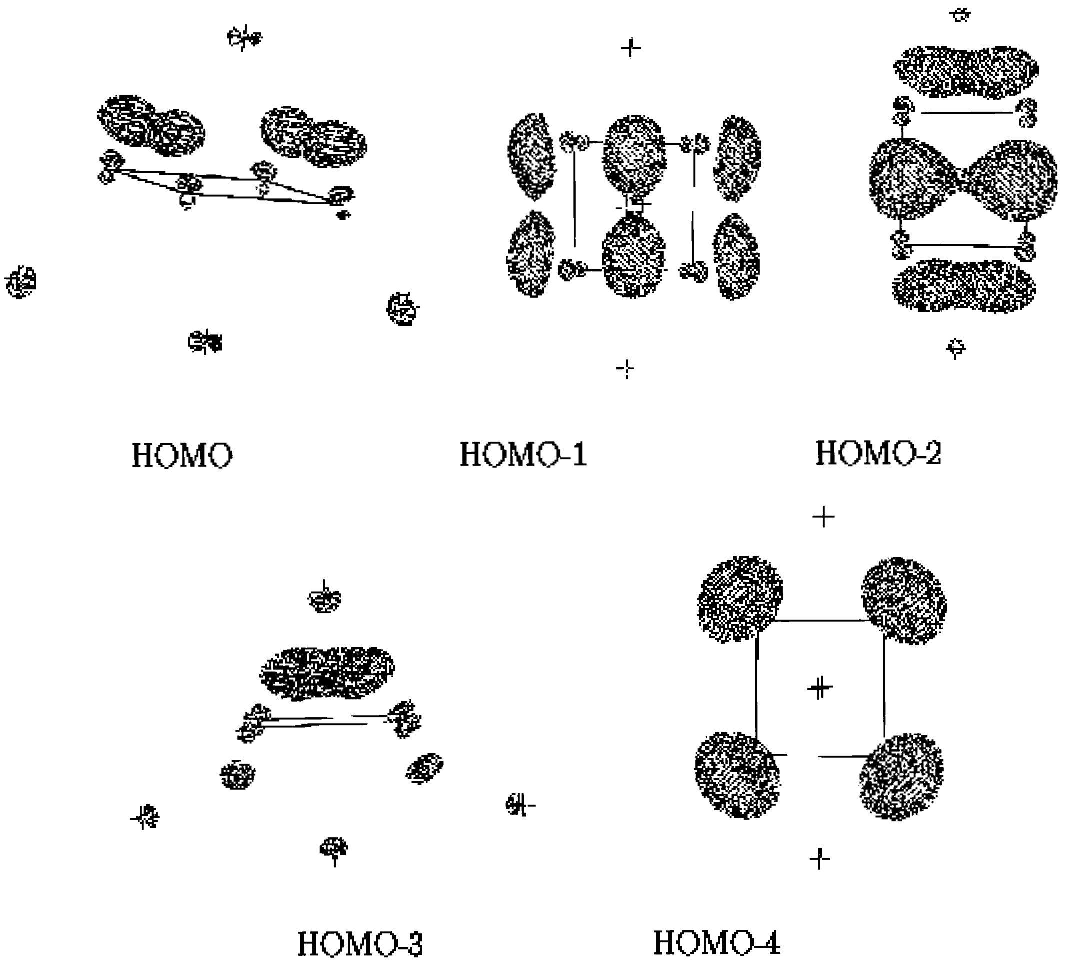


Figure 2. The last five HOMO pictures of the Al_4Na_4 cluster are shown. HOMO shows a localized and alternate π orbital in the Al_4 plane. HOMO-1 is a trans-annular bonding between the two pairs of σ bonds Al−Al and also the lone pair of electrons. HOMO-2 is a trans-annular bonding between the pair of σ orbitals of Al−Al. HOMO-3 is a trans-annular bonding between the two π orbitals of the Al−Al bonds. HOMO-4 shows a lone pair of electrons on 4 Al atoms.

TABLE 2: Bond Angles and the Dihedral Angles of the Optimized Ground State of Al_4Na_4 and $Al_4Na_3^-$ Clusters[a]

	angles in degrees	
	bond	dihedral
Al(1)−Al(2)-Al(4)	90.0 (90.0)	
Al(1)−Al(3)-Al(4)	90.0 (90.0)	
Al(2)−Al(4)-Al(3)	90.0 (90.0)	
Al(1)−Al(3)-Al(4)−Al(2)		0.0 (0.0)
Na(5)−Na(7)-Na(6)	154	
Na(8)−Al(1)−Al(2)−Al(4)[b]		61.11 (58.28)

[a] Bond angles and the dihedral angles of the $Al_4Na_3^-$ cluster are given in parentheses. [b] Shows the angle between the Na atom and the Al_4 plane.

TABLE 3: The Energies and the Difference between the HOMO and the LUMO for Ground and Excited States of the Al_4Na_4 Cluster and the Ground State of the $Al_4Na_3^-$ Cluster Obtained through Coupled-Cluster Calculations

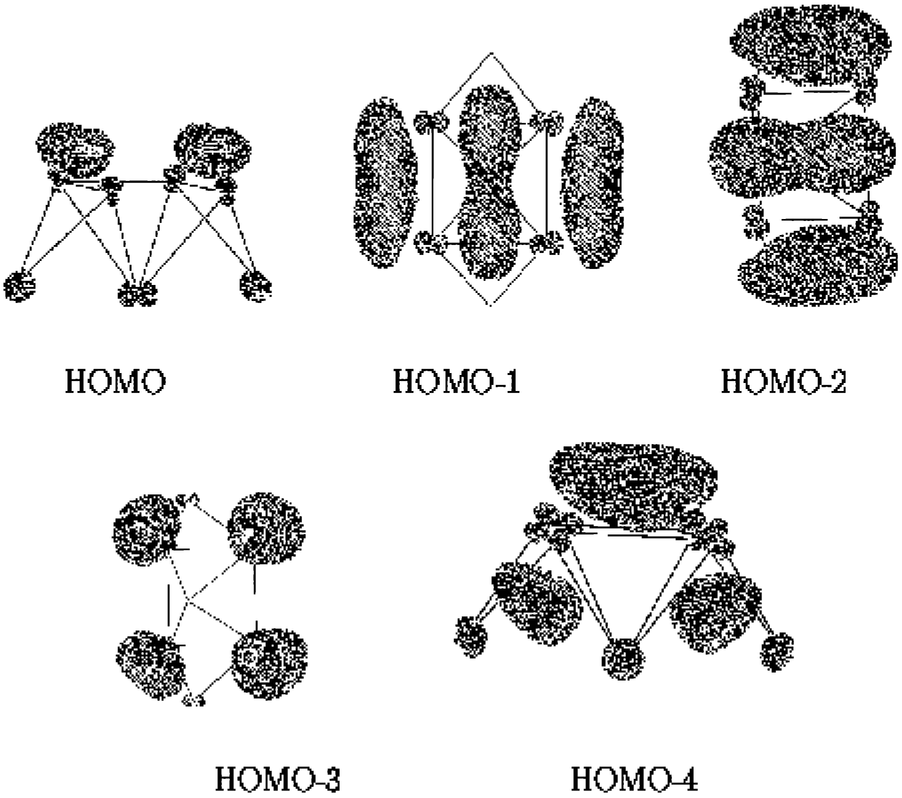
metal clusters	total energies (hartree)	HOMO−LUMO gap (eV)	ΔE^a (kcal/mol)
Al_4Na_4 (ground state)	−1615.2049	4.042	0.00
Al_4Na_4 (excited state)		4.228	4.35
$Al_4Na_3^-$ (ground state)	−1435.0128	1.240	0.00

[a] ΔE refers to the difference between the ground state and the excited-state energies.

Oppenhiemer molecular dynamics (BOMD) simulations.[11] The BOMD technique is based on the Kohn−Sham formulation of density functional using damped equations of motion to calculate the Al_4Na_4 cluster. Simulated annealing technique is used to obtain the equilibrium geometries.[11] The structures were considered to be converged when the forces on all the atoms were less than 10^{-5} eV/Å. The $Al_4Na_3^-$ structure was obtained by removing one Na atom and adding one negative charge. These structures were reoptimized using Moller−Plesset perturbation theory (MP2) with 6/31G(d,p) basis sets. Further, the clusters were refined using the coupled-cluster method with double excitations only (CCD)/6-31G(d,p),[12,13]

Results and Discussion

Before we discuss the results on bonding, we present the ground-state geometry of the Al_4Na_4 and $Al_4Na_3^-$ clusters. Tables 1 and 2 present the geometry of Al_4Na_4 and $Al_4Na_3^-$ clusters in the ground state. Table 3 presents the total energies and the gap between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) of the ground state and excited state of the Al_4Na_4 cluster. The total energy of the ground state of the $Al_4Na_3^-$ cluster is also presented in the Table 3. We found that the ground-state geometry obtained from the ab initio calculations, viz., MP2/


HOMO HOMO-1 HOMO-2

HOMO-3 HOMO-4

Figure 3. The last five HOMO pictures of $Al_4Na_3^-$ cluster are shown. HOMO shows localized and alternate π orbitals in the Al_4 plane. HOMO-1 is a trans-annular bonding between the two pairs of σ bonds of Al−Al. HOMO-2 is a trans-annular bonding between the two Al−Al bonds and also a lone pair of electrons. HOMO-3 is a trans-annular bonding of π character. HOMO-4 shows localized π bonds on Al−Al and a delocalized π electron density.

CCD for Al_4Na_4 (Figure 1a) is a capped octahedron (C_{2v} symmetry). The four Al atoms form a rectangular planar structure (D_{2h} symmetry) with two of its bond lengths being 2.680 Å and the other two being 2.852 Å (Table 1). The rectangular planar Al_4 structure found in the Al_4Na_4 cluster is similar to the Al_4 structure found in the Al_4Li_4 cluster studied earlier.[9,10] The excited-state geometry of Al_4Na_4 (Figure 1b) is seen to form a quinted roof with a buckled Al_4 unit and is 4−5 kcal/mol (Table 3) higher in energy than the ground state. However, the ground-state Al_4Na_4 structure obtained through BOMD calculations reported earlier[11] showed that the Al_4 species is buckled (Figure 1b), which is in contrast to the ab initio calculations studied in the present work. The ground-state geometry of the $Al_4Na_3^-$ cluster (Figure 1c) is also a capped octahedron (C_{2v} symmetry). The $Al_4Na_3^-$ system, having rectangular planar Al_4 structure (D_{2h} symmetry), is similar to the Al_4 structure found in the Al_4Na_4 cluster, with the only difference being that the shorter Al−Al bond is 2.288 Å and the longer Al−Al bond is 2.443 Å (Table 1), unlike the slightly distorted rectangular Al_4 structure in $Al_4Li_3^-$ cluster.[10] This is due to the symmetric capping of the three Na atoms. It is also seen from Table 1 that the Al_4 unit gets more contracted in the anion than in the neutral species. We have also carried out spin-polarized calculations for the Al_4Na_4 and $Al_4Na_3^-$ systems, and it was found that the singlet state is more stable than the triplet state.

The hybridization of the four Al atoms in the Al_4Na_4 and $Al_4Na_3^-$ clusters may be considered as sp^2, leaving one empty unhybridized p orbital on each Al atom in the Al_4 species. Although the difference in the ionization potential of Al and the Na atoms is very small, earlier studies have shown that in these classes of heteroclusters, the more electronegative atom occupies the interstitial position and behaves as a single entity or superatom.[11,14] In the present study, the Al_4 species in the Al_4Na_4 and $Al_4Na_3^-$ clusters behaves as a superatom and hence the electron affinity of the Al_4 species increases compared to the alkali atoms. This arrangement of the Al_4 species in Al_4Na_4 and $Al_4Na_3^-$ clusters allows the Na atoms to donate one electron to the unoccupied p_z orbital of the four Al atoms, thus providing the required 4 π electrons for antiaromaticity. The HOMO picture (Figure 2) clearly shows two localized π bonds along the two Al atoms having shorter bond lengths (2.68 Å) of the Al_4 unit in the Al_4Na_4 cluster. HOMO-1 (Figure 2) is mainly a trans-annular bonding between the pair of σ bonds of Al−Al atoms and lone pair of electrons of π character is seen. This kind of trans-annular bonding was also seen in the $Ga_4H_2^{2-}$ compound.[15] HOMO-2 (Figure 2) also shows a similar kind of trans-annular bonding between the pair of Al−Al bonds having higher bond lengths. HOMO-3 (Figure 2) also shows a trans-annular bonding, but it is seen between the π orbitals of the pair of Al−Al bonds. HOMO-4 (Figure 2) shows a lone pair of electrons on the four Al atoms. The two localized π bonds in the HOMO of the Al_4Na_4 cluster (Figure 2) arise due to the 4 π electrons donated by the four Na atoms to the Al_4 species, which is consistent with the charge transfer from the Na atoms to the Al atoms. We also see from Table 3 that the difference in the energy of the HOMO and the LUMO of the Al_4Na_4 ground state and the excited state is almost the same.

Interestingly, the bonding nature in the $Al_4Na_3^-$ cluster is similar to that in the Al_4Na_4 cluster. The HOMO (Figure 3) of $Al_4Na_3^-$ is the same as the HOMO (Figure 2) of the Al_4Na_4 cluster with alternate π bonds along the shorter Al−Al (2.288 Å) bonds. HOMO-1 (Figure 3) has a trans-annular bonding of σ bond character with lone pair of electrons similar to HOMO-1 of Al_4Na_4 system. HOMO-2 (Figure 3) of $Al_4Na_3^-$ has a trans-annular bonding between the two Al−Al bonds and also a

π-type lone pair of electrons showing a strong resemblance to the HOMO-2 (Figure 2) of Al_4Na_4. HOMO-3 shows a lone pair of electrons on Al atoms. HOMO-4 (Figure 3) shows localized π bonds along the shorter Al−Al bonds in the Al_4 species, but surprisingly, a delocalized orbital is also seen within the four Al atoms. The HOMO−LUMO gap in $Al_4Na_3^-$ gap is much less compared to the neutral species.

We have also performed the above calculations on the Al_4^{4-} system (not shown). Surprisingly, the calculations show that the Al_4^{4-} system was highly unstable. We do agree with the fact that, like the instability of the Al_4^{2-} system discussed earlier,[15] the instability in the Al_4^{4-} system is due to the Coulombic repulsion from the four negative charges on Al_4^{4-}. This indicates that the presence of the 4 Na^+ and 3 Na^+ cations in the Al_4Na_4 and $Al_4Na_3^-$ cluster, respectively, is required for the stability of the Al_4^{4-} species.

The preference of the rectangular geometry of Al_4 species in Al_4Na_4 and $Al_4Na_3^-$ cluster, which is a singlet state, as discussed earlier, is due to the mixing of energetically close states (pseudo-Jahn−Teller or second-order Jahn−Teller effect).[4a,16] This can also be explained by the fact that the distortion of the π electrons drives the molecule to bond-alternated geometry where short and localized π bonds can be achieved.[17]

Conclusion

Our investigation shows that the Al_4 species in the neutral Al_4Na_4 and anion $Al_4Na_3^-$ system has 4 π electrons with a planar rectangular geometry (singlet state) and two localized π bonds. Analogous to Al_4Li_4 and $Al_4Li_3^-$,[10] the present discussion demonstrates that the neutral Al_4Na_4 and anion $Al_4Na_3^-$ clusters are metal cyclodienes and are strong candidates for metallo-antiaromaticity. Thus, the present investigation and the earlier studies[10] show that the antiaromatic behavior is not only confined to the organic compounds but is also possible in the metal compounds. These studies on the existence of metallo-antiaromatic compounds would motivate the experimentalists to understand the chemical properties such as stability, reactivity, and magnetic properties and to compare them with the antiaromatic organic compounds.

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