Stability, Reactivity, and Aromaticity of Compounds of a Multivalent Superatom

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In this article, we analyze the stability, reactivity, and possible aromatic behavior of two recently reported clusters (Reveles, J. U.; Khanna, S. N.; Roach, P. J.; Castleman, A. W., Jr. *Proc. Natl. Acad. Sci*. **2006**, *103*, 18405), viz., Al_7C^- and Al_7O^- in the light of the principles of the maximum hardness and minimum electrophilicity as well as the nucleus-independent chemical shift values. Stability of these clusters in the context of addition/removal of an electron or an Al atom is now clearly understood.

Introduction

Aromaticity is the property of a planar, cyclic, conjugated molecule such as benzene, which is linked with its extraordinary stability and unusual reactivity pattern. This type of molecule is chemically more stable and possesses an appreciable amount of local magnetic field and with $(4n + 2)$ π electrons, in comparison to a nonaromatic counterpart, while the associated antiaromatic molecule is chemically more reactive having $4n - \pi$ electrons.[1−3] The electron delocalization described by resonance enhances the stability of the aromatic systems. Although the concept of aromaticity has been known for more than a century, it has not been provided us with a precise definition mainly owing to the fact that there are different characteristics that are often tested in determining the aromaticity of a molecule, which by itself is neither an experimentally observed quantity nor a theoretically defined quantity. Even sometimes two characteristics contradict each other.

Very recently, the aromaticity concept has been extended to the all-metal compounds[4−8] such as various cluster anions of Al, Ga, In, Hg, Sn, Si, and so forth as well as polyacene analogues of inorganic ring compounds including Na_6 through photoelectron spectroscopy measurement and/or theoretical calculations. The aromaticity/antiaromaticity of those systems as well as their complexes are yet to be properly understood in the light of the various existing aromaticity rules. Unlike the organic hydrocarbons such as benzene and cyclobutadiene, the energy levels of all-metal cluster molecules are closely placed and do not allow us to have an easy $\sigma-\pi$ separation and to develop a Hückel-type molecular orbital theory of $\pi-$only part of these molecules. Accordingly, both the π and σ aromaticities are to be considered for these molecules.

The Al_4^{2-} dianion and its complexes MAl_4^{2-} (M = Li, Na, K, Cu) are synthesized and investigated[4] through a negative ion photoelectron spectroscopy using a laser vaporization source that is supported by ab initio calculations. In all of these molecules, a square-planar Al_4^{2-} unit is present and is linked with the M^+ cation in its surroundings supporting various point group symmetries. It is argued that the presence of two delocalized π electrons in the Al_4^{2-} dianion makes it aromatic by obeying Hückel's $(4n + 2)\pi$ electron rule, which is authenticated by its planar and square structure (due to delocalization) in all of the MAl_4^{2-} species. It has also been theoretically studied[4] and shown that the presence of the Al_4^{2-} unit in some neutral M_2Al_4 molecules is conspicuous. Theoretical calculations have also shown[5] the transformation of nonaromatic $Al_4Cl_4(NH_3)_4$ into a π-aromatic $Na_2Al_4Cl_4(NH_3)_4$ molecule. High-level ab initio calculation of electron affinities of Al_n clusters has highlighted[8] that Al_4^{2-} is much more aromatic than the prototypical aromatic organic molecule, benzene. While the latter with only π aromaticity possesses two resonating Kekule structures, the former with the three independent delocalized π and σ bonding aromatic systems, separately obeying the $(4n + 2)$ rule, gives rise to 64 Kekule-like structures and because of this overwhelming resonance stabilization from both σ and π aromaticities the delocalization energy of Al_4^{2-} is much larger than that of benzene. Oxygen,[12,13] carbon,[13] and halogen[12,13] compounds of various Al_n clusters have been studied extensively in recent years.

All-metal antiaromatic molecule Al_4^{4-} is argued[7] to be present in $Li_3Al_4^-$ with a rectangular form, produced by laser vaporization and analyzed by using photoelectron spectroscopy and ab initio calculations. It is shown that the minimum energy structure of $Li_3Al_4^-$ contains a rectangular Al_4^{4-} tetraanion, which is Hückel antiaromatic because of the presence of 4π electrons ($4n$ rule) and is stabilized by three Li^+ ions. It is also shown[7] that Al_4^{4-} is π-antiaromatic and σ-aromatic at the same time. Antiaromaticity in the Al_4^{4-} is also theoretically shown[14] to be stabilized by Na^+ counterions in Na_4Al_4 and $Na_3Al_4^-$ clusters. Although the Al_4^{4-} is prescribed[15] through its electron localization function analysis to be overall antiaromatic, it is considered to be net aromatic[16,17] because its σ-aromaticity overwhelms its π-antiaromaticity as is obtained through its calculated nucleus-independent chemical shift (NICS)[16] and magnetic-field-induced current density[17] values. Similar theoretical analysis on aromatic hydro−metal systems is performed.[18] Stabilization of "antiaromatic" Al_4^{4-} through the formation of transition-metal complexes is analyzed[8] in terms of the calculated energy and NICS values. Other known all-metal aromatic compounds include Hg_4^{6-}, Ga_4^{2-}, and In_4^{2-}, whereas the antiaromatic compounds include Sn_6^{2-}, Si_6^{2-}, and Si_{12}^{2-}. Aromaticity and antiaromaticity in other silicon clusters are also reported.

In a recent issue of *Chemical & Engineering News*,[19] it is highlighted that an Al_7^- cluster mimics the behavior of a single multivalent germanium atom. S. N. Khanna and his group[13] have been involved in an important area of research involving the

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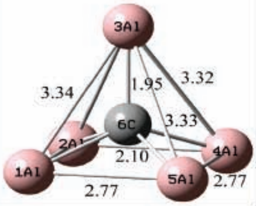
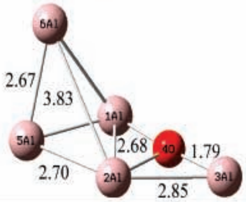
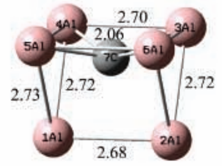
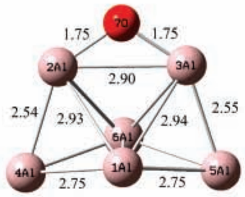
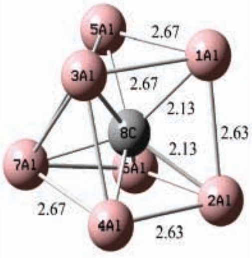
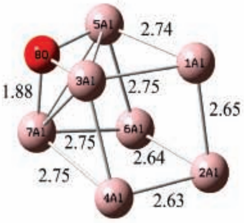
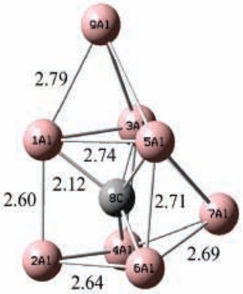
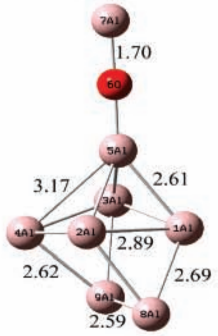
TABLE 1: Selected Geometrical Parameters (Bond Lengths, A) of Different Al$_n$C$^-$ and Al$_n$O$^-$ Clusters

Clusters	Bond length (A°)	Clusters	Bond length (A°)
Al$_5$C$^-$  	R(1,2) 2.78 R(1,5) 2.77 R(1,6) 2.10 R(2,4) 2.78 R(2,6) 2.10 R(3,6) 1.95 R(4,5) 2.77 R(4,6) 2.10 R(5,6) 2.10	**Al$_5$O$^-$**  	R(1,2) 2.68 R(1,4) 1.81 R(1,5) 2.50 R(1,6) 2.99 R(2,3) 2.85 R(2,4) 2.06 R(2,5) 2.70 R(3,4) 1.79 R(5,6) 2.67
Al$_6$C$^-$  	R(1,2) 2.68 R(1,4) 2.72 R(1,5) 2.73 R(2,3) 2.72 R(2,6) 2.72 R(3,4) 2.70 R(3,6) 2.98 R(3,7) 2.06 R(4,5) 2.98 R(4,7) 2.06 R(5,6) 2.70 R(5,7) 2.06 R(6,7) 2.06	**Al$_6$O$^-$**  	R(1,2) 2.93 R(1,3) 2.94 R(1,4) 2.75 R(1,5) 2.75 R(1,6) 3.19 R(2,3) 2.90 R(2,4) 2.54 R(2,6) 2.93 R(2,7) 1.75 R(3,5) 2.55 R(3,6) 2.94 R(3,7) 1.75 R(4,6) 2.75 R(5,6) 2.75
Al$_7$C$^-$  	R(1,2) 2.63 R(1,3) 2.67 R(1,4) 3.59 R(1,5) 2.67 R(1,8) 2.13 R(2,4) 2.63 R(2,6) 2.63 R(3,4) 2.67 R(3,5) 2.85 R(3,8) 2.13 R(3,7) 2.85 R(4,5) 4.16 R(4,6) 3.59 R(4,7) 2.67 R(4,8) 2.13 R(5,6) 2.67 R(5,7) 2.85 R(5,8) 2.13 R(6,7) 2.67 R(6,8) 2.13	**Al$_7$O$^-$**  	R(1,2) 2.65 R(1,3) 2.75 R(1,5) 2.74 R(2,4) 2.63 R(2,6) 2.64 R(3,4) 2.74 R(3,5) 2.81 R(3,7) 2.82 R(3,8) 1.88 R(4,7) 2.75 R(5,6) 2.74 R(5,8) 1.88 R(6,7) 2.75 R(7,8) 1.88
Al$_8$C$^-$  	R(1,2) 2.60 R(1,3) 2.74 R(1,5) 2.74 R(1,8) 2.12 R(1,9) 2.79 R(2,4) 2.64 R(2,6) 2.64 R(2,8) 2.15 R(3,4) 2.72 R(3,5) 2.80 R(3,7) 2.80 R(3,8) 2.07 R(3,9) 2.94 R(4,7) 2.69 R(4,8) 2.10 R(5,6) 2.71 R(5,7) 2.81 R(5,8) 2.07 R(5,9) 2.95 R(6,7) 2.69 R(6,8) 2.11 R(7,8) 2.38	**Al$_8$O$^-$**  	R(1,2) 2.89 R(1,3) 2.62 R(1,5) 2.61 R(1,8) 2.69 R(2,4) 2.57 R(2,5) 2.61 R(2,8) 2.68 R(3,4) 2.72 R(3,5) 2.73 R(3,9) 2.68 R(4,5) 3.17 R(4,9) 2.62 R(5,6) 1.73 R(6,7) 1.70 R(8,9) 2.59

metal clusters visualized as super atoms, for example, Al$_{13}$, Al$_{13}^-$, and Al$_{14}^{2+}$ clusters possess characteristics akin to that of halogen, noble gas, and alkaline earth atoms, respectively. A multivalent superatom, Al$_7^-$, forms stable compounds such as Al$_7$C$^-$ and Al$_7$O$^-$, whose stability mimicks that of SiC and CO, respectively, through an appropriate shell filling as in the standard *aufbau prinzip*. Al$_7$C$^-$ also forms ionic compounds with alkali metals with hardly any distortion in the original cluster unit. They have adopted[13] a joint experimental−theoretical approach to synthesize these clusters and to study their properties including the gap between the associated frontier orbitals as is the standard practice in the metal cluster studies.

TABLE 2: Total Energy (E, au), Frontier Molecular Orbital Energies (E_{HOMO}, E_{LUMO}, au), Hardness (η, eV), Electronegativity (χ, eV), and Electrophilicity (ω, eV) of Al_7C^- and Al_7O^- and Their Ions

cluster	E	E_{HOMO}	E_{LUMO}	χ	η	ω
Al_7C	−1735.246	−0.207	−0.139	4.705	0.935	11.839
Al_7C^-	−1735.364	−0.067	0.030	0.515	1.318	0.100
Al_7C^{2-}	−1735.288	0.091	0.165	−3.492	1.010	6.039
Al_7O	−1772.483	−0.189	−0.125	4.278	0.877	10.437
Al_7O^-	−1772.577	−0.047	0.026	0.272	0.993	0.037
Al_7O^{2-}	−1772.509	0.092	0.140	−3.165	0.653	7.672

Popular qualitative concepts such as electronegativity,[20,21] hardness,[22,23] electrophilicity,[24] and so forth have been used in analyzing chemical bonding, stability, reactivity, and interactions. Conceptual density functional theory[25] (CDFT) provides theoretical bases for these concepts as well as the associated electronic structure principles, such as the electronegativity equalization principle (EEP),[26] the hard−soft acids and bases (HSAB) principle,[27] the maximum hardness principle (MHP),[28] the minimum polarizability principle (MPP),[29] the minimum electrophilicity principle (MEP),[30] the minimum magnetizability principle (MMP),[31] and so forth. These principles have been utilized[8−11] in the past in analyzing aromaticity/antiaromaticity in Al_4^{2-}/Al_4^{4-} and their various complexes, benzene/cyclobutadiene, and polyacene analogues of several inorganic ring compounds including Na_6.

In the present work, we analyze the exceptional stability of Al_7C^- and Al_7O^- when the number of electrons and/or the number of Al units are changed by using various electronic structure principles and the nucleus-independent chemical shift calculated at the ring center, NICS(0), which is an indicator of the aromatic/antiaromatic behavior.

Theoretical Background

Conceptual density functional theory[25] provides definitions of global descriptors such as electronegativity[20,21] (χ), hardness[22,23] (η), and electrophilicity[24] (ω) as

$$\chi = -\,(\partial E/\partial N)_{\upsilon(\vec{r})} = -\mu \tag{1}$$

$$\eta = \frac{1}{2}\,(\partial^2 E/\partial N^2)_{\upsilon(\vec{r})} \tag{2}$$

and

$$\omega = \chi^2/2\eta \tag{3}$$

for an N-electron system with $\upsilon(\vec{r})$ and μ as the external and chemical potentials, respectively.

For analyzing the site selectivity in a molecule, we define the local descriptors such as the Fukui function [32](f_k^α) and the philicity [33](ω_k^α) in terms of the respective electronic population, p_k, at atom k as

$$f_k^+ = p_k(N+1) - p_k(N) \text{ for nucleophilic attack} \tag{4a}$$

$$f_k^- = p_k(N) - p_k(N-1) \text{ for electrophilic attack} \tag{4b}$$

$$f_k^0 = \frac{1}{2}\,(f_k^+ + f_k^-) \text{ for radical attack} \tag{4c}$$

and $\omega_k^\alpha = \omega . f_k^\alpha$, $\alpha = +, -, 0$ denotes nucleophilic, electrophilic ,and radical attacks, respectively.

Using a finite difference method, the working equations for the calculation of chemical potential, electronegativity, and chemical hardness can be given by

$$\mu = -\frac{IP + EA}{2};\ \chi = \frac{IP + EA}{2};\ \eta = \frac{IP - EA}{2} \tag{5}$$

where IP and EA are the ionization potential and electron affinity of the system, respectively.

Using the ΔSCF finite difference approach, the IP and EA can be calculated for the N-electron system as follows

$$IP = E(N-1) - E(N);\ EA = E(N) - E(N+1) \tag{6}$$

where $E(N)$ is the electronic energy for the N-electron system.

If E_{HOMO} and E_{LUMO} are the energies of the highest-occupied and lowest-unoccupied molecular orbitals, respectively, then eq 5 can be rewritten using Koopmans' theorem as

$$\mu = \frac{E_{HOMO} + E_{LUMO}}{2};\ \chi = -\frac{E_{HOMO} + E_{LUMO}}{2};\ \eta = \frac{E_{LUMO} - E_{HOMO}}{2} \tag{7}$$

For a stable system or a favorable process, the hardness often becomes the maximum and the electrophilicity becomes the minimum in most cases. To test the validity of these principles vis-à-vis the exceptional stability of Al_7C^- and Al_7O^-, we calculate various global and local descriptors.

Computational Details

Geometries of Al_nC^- and Al_nO^- are optimized at the B3LYP/6-311+G** level of theory. The global quantities χ, η, and ω are calculated using a finite difference approximation (eq 5) and Koopmans' theorem (eq 7) along with eq 3. The imaginary frequency (NIMAG) is zero for all different Al_nC^- and Al_nO^- clusters. The f_k^α value is calculated by using eq 4, and the ω_k^α value is calculated by the equation $\omega_k^\alpha = \omega . f_k^\alpha$. We calculate the stability of different clusters by the following equation

$$\Delta E = E(Al_{n-1}Y^-) + E(Al) - E(Al_nY^-) \tag{8}$$

where Y = C,O and E is the total energy of clusters.

Necessary charges are obtained using a natural population analysis (NPA) scheme. The aromatic behavior is analyzed using the NICS (0) values.

Results and Discussion

Table 1 provides the optimized geometries and selected bond lengths of Al_nC^- and Al_nO^- where n = 5−8. All of the systems studied here correspond to minimum energy structures on the potential energy surface as authenticated by the number of imaginary frequency to be zero. C is endohedral in Al_7C^-, and

TABLE 3: Nucleus-Independent Chemical Shift (NICS (0), ppm) Values of Various Rings in Al_7C^- and Al_7O^-

cluster	ring	ring	ring	ring	ring	ring	ring
	1 2 4 3	4 2 6 7	1 2 6 5	1 3 5	3 5 7	5 6 7	3 4 7
Al_7C^-	−66.663	−66.664	−66.728	−54.993	−52.973	−54.988	
Al_7O^-	−43.058	−42.981	−43.067	−38.423	−45.411	−35.955	−36.875

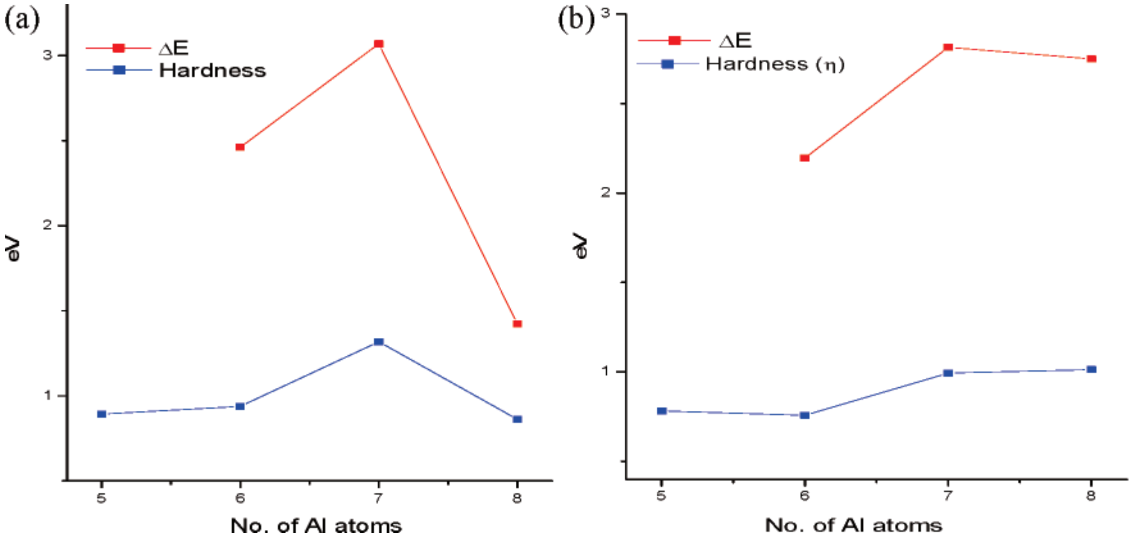


Figure 1. Plots of hardness and ΔE of (a) Al_nC^- and (b) Al_nO^- clusters.

TABLE 4: Total Energy (E, au), Frontier Molecular Orbital Energies (E_{HOMO}, E_{LUMO}, au), Electronegativity (χ, eV), Hardness (η, eV), and Electrophilicity (ω, eV) of Different Al_nC^- and Al_nO^- Clusters

cluster	E	E_{HOMO}	E_{LUMO}	ΔE^a	χ	η	ω
Al_5C^-	−1250.39	−0.032	0.034		−0.031	0.893	5E−04
Al_6C^-	−1492.86	−0.055	0.014	2.462	0.558	0.938	0.166
Al_7C^-	−1735.36	−0.067	0.030	3.070	0.515	1.318	0.100
Al_8C^-	−1977.80	−0.047	0.016	1.424	0.425	0.862	0.105
Al_5O^-	−1287.62	−0.016	0.041		−0.345	0.782	0.076
Al_6O^-	−1530.09	−0.034	0.021	2.194	0.179	0.757	0.021
Al_7O^-	−1772.58	−0.047	0.026	2.813	0.272	0.993	0.037
Al_8O^-	−2015.06	−0.047	0.027	2.749	0.273	1.013	0.037

[a] $\Delta E = E(Al_{n-1}Y^-) + E(Al) - E(Al_nY^-)$; Y = C,O.

O is exohedral in Al_7O^- as was pointed out by Reveles et al.[13] Although most of the bond lengths of Al_7C^- and Al_7O^- obtained in the present work match with those reported in ref 13, there are marked deviations in some cases, for example, $R(7,8)$ in Al_7O^- is 1.88 A in the present work and is 1.92 A in ref 13, which might have originated from different levels of calculations. They[13] have used the de Mon2k package[34] for DFT calculation with the generalized gradient approximation-type exchange-correlation functional given by Perdew et al.[35] Even they have noticed similar variations in bond lengths[13] for different levels of computation. We compare our results (bond lengths) for Al_7O (not shown here) with those calculated by Sun et al.[12] at B3LYP/6-311G(2d) level, and they match very well.

The energy (E), frontier orbital energies (E_{HOMO}, E_{LUMO}), electronegativity (χ), hardness (η), and electrophilicity (ω) values for $X(Al_7C^-)$, $Y(Al_7O^-)$, and their ions are provided in Table 2. The χ values of X and Y when compared to those values of $X^{\pm}$ and $Y^{\pm}$ suggest that although $X^+(Y^+)$ prefers to take an electron, X(Y) does not like to take it that much. The χ values of X^- and Y^- are negative, suggesting the difficulty associated with the further electron intake. The stability of X and Y is clearly delineated through their E, η, and ω values. While the E and ω values of X (Y) are the lowest, the η value is the highest when compared to those values of $X^{\pm}$ ($Y^{\pm}$) as predicted by the principles of minimum energy and electrophilicity and maximum hardness. To check the corresponding ΔSCF values (without using Koopmans' approximation), we found that (η, ω) values for X [Y] are (1.315, 0.030) [(1.106, 0.014)] and comparable to those values reported in Table 2.

The NICS (0) values associated with various rings of Al_7C^- and Al_7O^- are presented in Table 3. Corresponding large negative values (NICS (0) value of benzene is −9.7) indicate[16] that the highly aromatic nature of these clusters is expected from such a stable ring compound.

The above analysis confirms the fact that Al_7C^- and Al_7O^- are more stable when compared with the respective species obtained through electron addition/removal. Now we study whether Al_7C^- and Al_7O^- are also more stable when compared with the stability of their neighbors Al_nY^-, n = 5,6,8, Y = C,O. Table 4 presents the total energy, energies of the HOMO and the LUMO, ΔE (eq 8), electronegativity, hardness, and electrophilicity of these clusters. Figure 1 depicts the variation of ΔE and η with the number of Al atoms present in the cluster. It clearly delineates the stability of Al_7C^- and Al_7O^- in comparison to their neighbors as dictated by the principles of minimum energy and maximum hardness through the respective peaks at n = 7. Although the numerical values differ slightly with those reported by Reveles et al.[13] because of the difference in the level of calculation, the qualitative trends remain more or less similar and Al_7C^- and Al_7O^- are more stable than their neighbors.

The NPA charges and philicities at various atomic centers of Al_7C^- and Al_7O^- are presented in Table 5. In Al_7C^-, all Al

TABLE 5: Charges (q_k(NPA)) and Philicity(ω_k^{α}) on Various Atoms in Al_7C^- and Al_7O^-

atom	no.	q_k	ω_k^+	ω_k^-	ω_k°	atom	no.	q_k	ω_k^+	ω_k^-	ω_k°
Al	1	0.291	0.012	0.017	0.014	Al	1	−0.192	0.008	0.009	0.009
Al	2	0.191	0.019	0.019	0.019	Al	2	−0.269	0.003	0.001	0.002
Al	3	0.295	0.018	0.011	0.015	Al	3	0.481	0.004	0.002	0.003
Al	4	0.289	0.012	0.015	0.014	Al	4	−0.199	0.004	0.009	0.007
Al	5	0.297	0.019	0.013	0.016	Al	5	0.472	0.001	0.002	0.002
Al	6	0.294	0.012	0.017	0.014	Al	6	−0.195	0.006	0.009	0.008
Al	7	0.295	0.019	0.012	0.015	Al	7	0.498	0.010	0.002	0.006
C	8	−2.954	−0.010	−0.003	−0.007	O	8	−1.596	−8E−05	0.002	7E−04

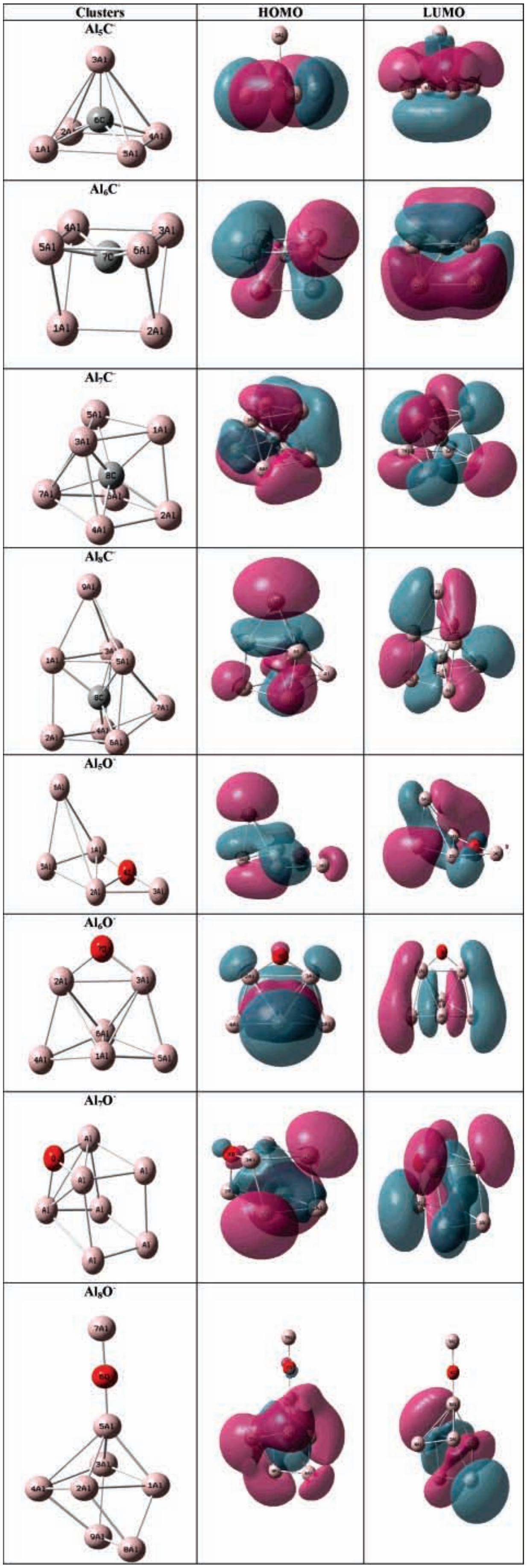


Figure 2. Optimized geometries (B3LYP/6-311+G**) and frontier molecular orbitals of different Al_nC^- and Al_nO^- clusters.

atoms are preferred sites for attack by an anion or a hard nucleophile,[36] whereas the C center is apt for an attack by a cation or a hard electrophile. The O center and Al (1, 2, 4, 6) atoms are good for attack by a cation/hard electrophile, whereas the rest of the Al atoms in Al_7O^- are appropriate for the attack by an anion/a hard nucleophile. The fact is corroborated by the respective plots of the highest-occupied and lowest-unoccupied molecular orbitals (Figure 2). For the comparison, the frontier orbitals of other clusters are also presented. Philicity values provide the corresponding information regarding the attack by a soft species. Although numerical calculations[37] might show that in some cases the minimum Fukui function (FF)[38] sites are the best for the hard−hard interactions and the charges may fail to identify those sites due to the intrinsic inadequecies associated with density partitioning,[39] the least reactive sites[32] having the minimum FF values may counter the Klopman dictum[36] of the charge-controlled hard reactions as well as the original definition of FF.[32] The minimum FF condition may, however, be used for a level playing field[40] for a dominantly charge-controlled reaction with two potential sites that are equally favorable electrostatically. For the soft−soft reactions with two equivalent sites, electrostatic potential may be used as a tie-breaker.[40]

Al_7C^- is more electrophilic than Al_7O^- because the former has a larger ω value. Although C and O centers are suitable for attack by a hard electrophile, those centers are bad as far as the attack of the soft electrophiles are concerned. Sites of preference for hard and soft nucleophiles are also not always the same. On an average, atomic sites in Al_7C^- are more reactive than those of Al_7O^-.

Concluding Remarks

Density functional theory calculations at the B3LYP/6-311+G** level suggest that both Al_7C^- and Al_7O^- are stable as dictated by the maximum hardness principle and the minimum electrophilicity principle. The NICS (0) values suggest their strong aromatic character. The stability of these clusters is noticed when it is compared with that of their neighbors formed by varying the number of electrons and/or Al atoms. Their site selectivity toward attack by ions and hard/soft electro-(nucleo) philes is analyzed in terms of atomic charges and philicities. Both C and O atoms are potent sites for attack by a cation or a hard electrophile but not as good for the attack by a soft electrophile.

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