Stability and Reactivity of All-Metal Aromatic and Antiaromatic Systems in Light of the Principles of Maximum Hardness and Minimum Polarizability

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It is demonstrated that among various possible isomers of all-metal aromatic compounds such as Al_4^{2-} and their complexes the most stable isomer with the minimum energy is the hardest and the least polarizable. A similar situation is observed for different isomers of all-metal antiaromatic compounds such as Al_4^{4-} and their complexes. It is shown that linear Al_4^{4-} is energetically more stable than its cyclic isomer. The reaction energies associated with the complexation processes highlight the stability of those complexes. The difference in energy, hardness, and polarizability between a cyclic molecule and its linear counterpart convincingly shows that an aromatic molecule exhibits negative changes in energy and polarizability but positive changes in hardness as expected from the principles of minimum energy, minimum polarizability, and maximum hardness. Although the aromaticity of Al_4^{2-} is unequivocally established through this study, the antiaromaticity picture in the case of Al_4^{4-} is shown to be poorly understood;however, the present analysis sheds light on this controversy.

Introduction

Kekulé[1] introduced the concept of aromaticity to explain the extraordinary stability of benzene, Pauling[2] explained aromaticity using quantum mechanics, and Hückel[3] tried to rationalize the same through his famous $(4n + 2)$ π-electron rule. This intriguing concept has occupied the minds of almost all researchers in chemistry over the ages.[4] An accepted definition[4,5] of aromaticity may be given as follows: "An aromatic molecule is one in which electrons are free to cycle around circular arrangements of atoms connected via identical bonds which are resonance hybrids of single and double bonds. It displays enhanced chemical stability compared to similar nonaromatic molecules and posseses significant local magnetic field, a planar structure, and $(4n + 2, n \geq 0)$ π-electrons in a single ring. On the other hand, an antiaromatic molecule contains $4n$ $(n \neq 0)$ π-electrons in a cyclic planar, or nearly planar, system of alternating single and double bonds".

Originally, the aromaticity concept was restricted to cyclic organic molecules with an occasional mention of inorganic molecules such as borazine (inorganic benzene). There has been a recent upsurge of interest in the field with the advent of aromaticity and antiaromaticity associated with metal clusters.[6−19] A series of bimetallic clusters with the chemical composition MAl_4^- (M = Li, Na, K, and Cu) are synthesized and investigated[6] through negative ion photoelectron spectroscopy using a laser vaporization source which is supported by ab initio calculations. In all of these molecules, a square planar Al_4^{2-} unit is present and is linked to the M^+ cation to give an overall pyramidal shape of MAl_4^-. It is argued that the presence of two delocalized π-electrons in the Al_4^{2-} dianion makes it aromatic by obeying Hückel's $(4n + 2)$ rule, which is authenticated by its planar and square structure (due to delocalization) in all the MAl_4^- species. Some neutral M_2Al_4 molecules have also been theoretically studied,[6] wherein the presence of Al_4^{2-} is shown to be conspicuous. Theoretical calculations have also shown[7] the transformation of a nonaromatic $Al_4Cl_4(NH_3)_4$ molecule 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. Although the latter with only π-aromaticity possesses two resonating Kekulé structures, the former with three independent delocalized π- and σ-bonding aromatic systems, separately obeying the $(4n + 2)$ rule, gives rise to 64 Kekulé-like structures. It has been shown[8] that the Al_3^- anion also exhibits both π- and σ-aromaticity with nine possible resonating structures.

The all-metal rectangular antiaromatic molecule Al_4^{4-} is argued[9] to be present in $Li_3Al_4^-$, 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 four π-electrons ($4n$ rule) and is stabilized by three Li^+ ions. It is also shown[9] that Al_4^{4-} is π-antiaromatic and σ-aromatic at the same time. Antiaromaticity in the Al_4^{4-} molecule is also theoretically shown[10] to be stabilized by Na^+ counterions in Na_4Al_4 and $Na_3Al_4^-$ clusters. Although Al_4^{4-} is prescribed[11] through its electron localization function (ELF) analysis to be overall antiaromatic, it is considered to be net aromatic[12,13] because its σ-aromaticity overwhelms its π-antiaromaticity, as is shown through its calculated nucleus independent chemical shift (NICS)[12] and magnetic field induced current density[13] values. The NICS (0) and NICS (1) are defined as the amount of absolute magnetic shielding calculated at the ring center and 1 Å above it, respectively. Similar theoretical analysis on aromatic hydro metal systems is performed.[14] All-metal aromatic compounds such as Hg_4^{6-}, Ga_4^{2-}, and In_4^{2-} [15] and antiaromatic[16]

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compounds such as Sn_6^{2-}, Si_6^{2-}, and Si_{12}^{2-} are also known. Aromaticity and antiaromaticity in other silicon clusters have been reported.[17] Complexation of all-metal aromatic[18] and antiaromatic[19] systems is studied at the RB3LYP/6-311G** level of theory. Stabilization of antiaromatic Al_4^{4-} through the formation of transition-metal complexes is analyzed[19] in terms of the calculated energy and NICS values.

Theoretical Background

Density functional theory (DFT)[20,21] has been quite successful in providing theoretical bases for popular qualitative chemical concepts introduced from time to time to explain chemical reactivity and selectivity, e.g., electronegativity,[22,23] chemical potential,[23] hardness,[24,25] and electrophilicity.[26] The hardness concept was introduced by Pearson through his famous hard−soft acid−base principle[24,25] which states that "hard likes hard and soft likes soft". Another hardness-based electronic structure principle is the maximum hardness principle (MHP),[27] which states that "there seems to be a rule of nature that molecules arrange themselves to be as hard as possible". Constancy of the chemical and external potentials is demanded by the MHP. A related principle is the minimum polarizability principle (MPP),[28,29] which states that "the natural direction of evolution of any system is towards the state of minimum polarizability".

In the present paper, we analyze the aromaticity and antiaromaticity of all-metal systems in light of the MHP and the MPP. A DFT (B3LYP/6-311+G*) calculation is performed to find out the energy (E) and polarizability (α) values. Also, the chemical hardness (η), the chemical potential (μ), and the electrophilicity index (ω) are calculated using both the Koopmans method and the ΔSCF method.

The quantitative definitions for the chemical potential (μ) and electronegativity (χ)[20] for an N-electron system with total energy E can, respectively, be given as

$$\mu = \left[\frac{\partial E}{\partial N}\right]_{v(\vec{r})} \tag{1}$$

and

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \tag{2}$$

where $v(\vec{r})$ is the external potential.

Chemical hardness (η) has been identified as a useful global reactivity index in atoms, molecules, and clusters.[20] The theoretical definition of chemical hardness has been provided by DFT as the second derivative of electronic energy with respect to the number of electrons (N) for a constant external potential $v(\vec{r})$, viz.,

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})} \tag{3}$$

Use of a finite difference method can give the working equations for the calculation of the chemical potential, the electronegativity, and the chemical hardness by

$$\mu = -\frac{\text{IP} + \text{EA}}{2} \qquad \chi = \frac{\text{IP} + \text{EA}}{2} \qquad \eta = \frac{\text{IP} - \text{EA}}{2} \tag{4}$$

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

Parr et al.[26] defined the electrophilicity index, which measures the stabilization in energy when the system acquires an additional electronic charge, ΔN, from the environment as

$$\omega = \frac{\mu^2}{2\eta} \tag{5}$$

If ϵ_{HOMO} and ϵ_{LUMO} are the energies of the highest-occupied and lowest-unoccupied molecular orbitals, respectively, then the above equations can be rewritten using Koopmans' theorem[20] as

$$\text{IP} \approx -\epsilon_{\text{HOMO}} \qquad \text{EA} \approx -\epsilon_{\text{LUMO}}$$

$$\chi = -\frac{\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}}{2} \qquad \eta = \frac{\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}}{2} \tag{6}$$

Electron affinity refers to the capability of a ligand to accept precisely one electron from a donor. However, in many kinds of bonding, viz., covalent, dative, or hydrogen bonding, partial charge transfer takes place. In those cases, ω becomes a better descriptor.

The electric dipole polarizability is a measure of the linear response of the electron density in the presence of an infinitesimal electric field, **F**, and it represents a second-order variation in energy

$$\alpha_{a,b} = -\left(\frac{\partial^2 E}{\partial \mathbf{F}_a \partial \mathbf{F}_b}\right) \qquad a,b = x,y,z \tag{7}$$

The polarizability α is calculated as the mean value, as given in the following equation

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{8}$$

Alternatively, using the ΔSCF finite difference approach, we can calculate the IP and EA for the N-electron system as follows:

$$\text{IP} \approx E(N-1) - E(N) \qquad \text{EA} \approx E(N) - E(N+1) \tag{9}$$

where $E(N)$ is the electronic energy for the N-electron system. Using the IP and EA values from eq 9, we can calculate the corresponding values of the chemical potential, the chemical hardness, and the electrophilicity index using eqs 4 and 5.

Results and Discussion

All-Metal Aromatic Molecule Al_4^{2-} and Its Family. Figure 1 presents the optimized structures of Al_4^{2-} with various symmetries such as $D_{\infty h}$, D_{3h}, D_{2h}, and D_{4h} and associated MAl_4^- (M = Li, Na, K, and Cu) compounds with different symmetries such as $C_{\infty v}$, C_{4v}, C_{2v}, and C_s. The Al_4^{2-} unit with $D_{\infty h}$, D_{3h}, D_{2h}, and D_{4h} point groups designated as A, B, C, D, and M_i, with i = 1, 2, 3, and 4, is used for Li, Na, K, and Cu, respectively. Two different ways of attachment of the metal ion to the Al_4^{2-} unit give rise to B1- and B2-, C1- and C2-, and D1- and D2-like structures whose explicit forms are depicted in Figure 1. The geometries of C, B1(M_i)C_{2v}, B2(M_i)C_{2v}, and C2(M_i)C_s are optimized with restrictions on the bond lengths, bond angles, and dihedral angles, as mentioned in the footnotes of Tables 1−5; otherwise, the optimization does not converge. The number of imaginary frequencies (NIMAG) is zero in all the unrestricted cases except $KAl_4^-(C_{\infty v})$. The geometry-constrained $Al_4^{2-}(D_{2h})$ is found with zero NIMAG, but in most cases, the geometry-constrained isomers are found with nonzero NIMAG, as expected. Nonzero NIMAG values are mentioned in the corresponding figures. It may be noted that nonzero NIMAG values are reported in the past for similar systems.[8,15]

Tables 1−5 show the energy, polarizability, hardness, chemical potential, and electrophilicity of Al_4^{2-} and MAl_4^- (M =

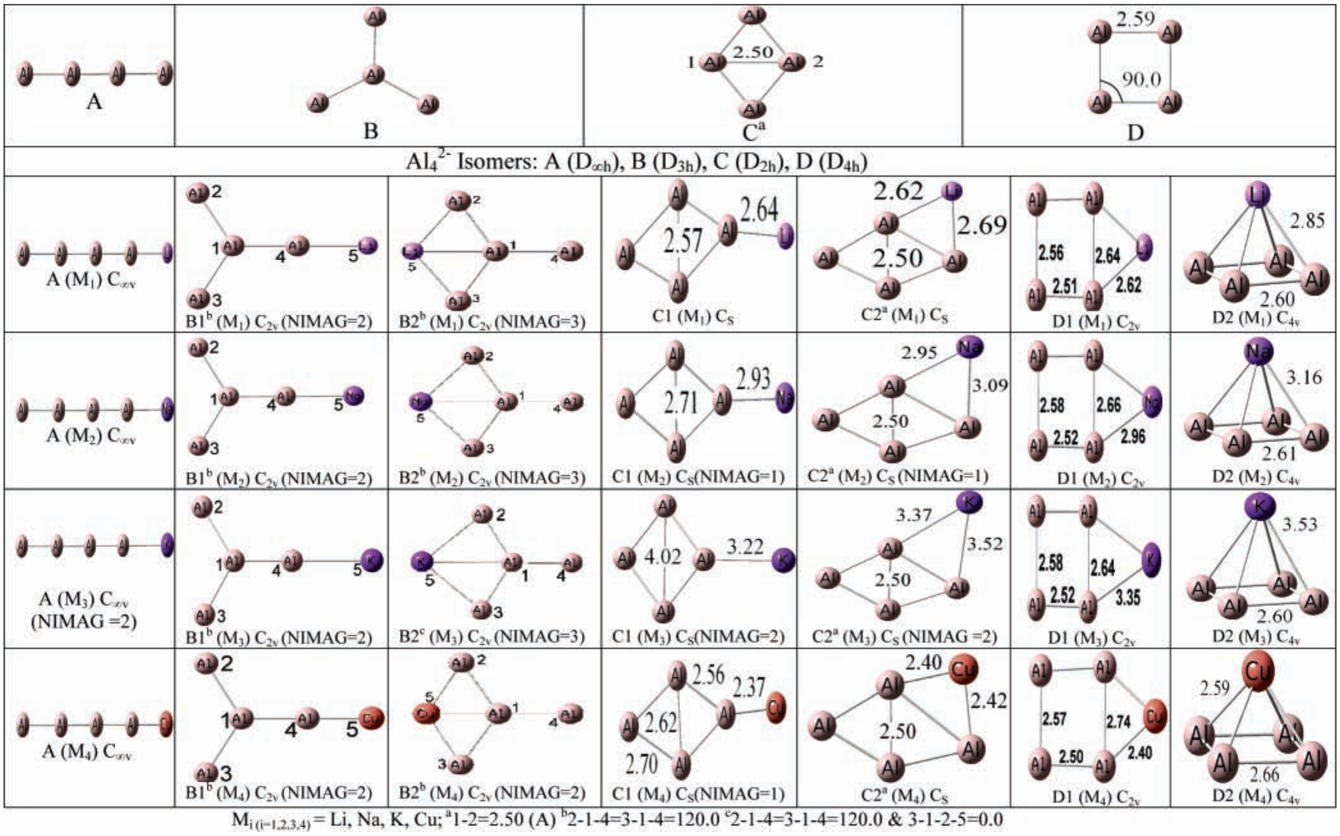


Figure 1. Optimized structures of various isomers of Al_4^{2-} and their MAl_4^- complexes (M = Li, Na, K, and Cu).

TABLE 1: Energy (*E*), Relative Energy (E_R), Polarizability (α), Hardness (*η*), Chemical Potential (*μ*), and the Electrophilicity (*ω*) Values of Different Isomers of Al_4^{2-}

				Koopmans[c]			ΔSCF[c]		
Al_4^{2-}	E^a	E_R^a	α^b	η	μ	ω	η	μ	ω
$D_{\infty h}$	−969.698	0.0425	675.82	0.5286	3.185	9.5955	1.5117	3.1058	3.1905
D_{3h}	−969.702	0.0382	665.29	0.7916	3.5802	8.0964	1.7408	3.4148	3.3495
D_{2h}^d	−969.692	0.0480	585.83	0.0812	3.7287	85.581	1.1299	3.6545	5.9102
D_{4h}	−969.740	0.0000	525.79	0.9773	3.8797	7.7008	1.9647	3.6248	3.3438

[a] In hartrees. [b] In atomic units (au). [c] In electronvolts (eV). [d] Geometrical constraint: 1−2 = 2.50 Å.

TABLE 2: Energy (*E*), Relative Energy (E_R), Polarizability (α), Hardness (*η*), Chemical Potential (*μ*), and the Electrophilicity (*ω*) Values of Different Isomers of $LiAl_4^-$

$LiAl_4^-$ cluster					Koopmans[c]			ΔSCF[c]		
Al_4^{2-}	$LiAl_4^-$	E^a	E_R^a	α^b	η	μ	ω	η	μ	ω
$D_{\infty h}$	$C_{\infty v}$	−977.278	0.084	686.38	0.380	−0.003	1E−05	1.273	−0.183	0.013
D_{3h}^d	C_{2v} 1	−977.294	0.068	618.58	0.446	0.082	0.008	1.387	−0.119	0.005
	C_{2v} 2	−977.312	0.050	428.34	0.685	0.159	0.018	1.750	−0.091	0.002
D_{2h}	C_s 1	−977.316	0.046	572.07	0.542	0.151	0.021	1.441	−0.138	0.007
	C_s 2^e	−977.331	0.030	406.02	0.482	0.157	0.025	1.526	−0.063	0.001
D_{4h}	C_{2v}	−977.357	0.005	414.45	0.838	0.235	0.033	1.765	−0.155	0.007
	C_{4v}	−977.362	0.000	375.03	1.011	0.350	0.061	3.622	1.633	0.368

[a] In hartrees. [b] In atomic units (au). [c] In electronvolts (eV). [d] Geometrical constraints: ∠1−2−4 = ∠3−2−4 = 120.0°. [e] Geometrical constraint: 1−2 = 2.50 Å.

Li, Na, K, and Cu) molecules. The last three quantities are reported for both Koopmans' and ΔSCF calculations. It may be noted that they provide different trends in some cases (Table 5) because of the breakdown of the Koopmans theorem. Corresponding reaction energies and NICS (0) and NICS (1) values of these molecules are presented in Tables 6 and 7, respectively.

It is observed that the Al_4^{2-} molecule can exist in three possible stable isomeric forms with point group symmetries $D_{\infty h}$, D_{3h}, and D_{4h}. Among these isomers, Al_4^{2-} with D_{4h} symmetry is found to be the energetically most stable, as reported by Li et al.[6] The D_{2h} isomer is not stable and hence is optimized with a geometrically constrained bond length (Figure 1). It is heartening to note that the D_{4h} isomer is the least polarizable and the hardest (both Koopmans' and ΔSCF results) and hence obeys the minimum polarizability and maximum hardness principles.

Although Al_4^{2-} with D_{3h} symmetry is stable, none of its MAl_4^- complexes are stable and are optimized with restrictions on bond lengths, bond angles, and dihedral angles. Their NIMAG values are nonzero in most cases. On the other hand, MAl_4^- complexes with C_s symmetry in a specific sense (C1-

TABLE 3: Energy (E), Relative Energy (E_R), Polarizability (α), Hardness (η), Chemical Potential (μ), and the Electrophilicity (ω) Values of Different Isomers of $NaAl_4^-$

$NaAl_4^-$ cluster					Koopmans^c			ΔSCF^c		
Al_4^{2-}	$NaAl_4^-$	E^a	$E_R{}^a$	α^b	η	μ	ω	η	μ	ω
$D_{\infty h}$	$C_{\infty v}$	−1132.063	0.081	719.79	0.370	−0.042	0.002	1.272	−0.192	0.014
$D_{3h}{}^d$	C_{2v} 1	−1132.080	0.064	641.89	0.476	0.062	0.004	1.426	−0.148	0.008
	C_{2v} 2	−1132.085	0.059	489.17	0.529	0.093	0.008	1.586	−0.099	0.003
D_{2h}	C_s 1	−1132.100	0.044	615.20	0.432	−0.036	0.002	1.366	−0.172	0.011
	C_s 2^e	−1132.109	0.035	462.98	0.458	0.127	0.018	1.484	−0.044	0.001
D_{4h}	C_{2v}	−1132.135	0.009	458.25	0.724	0.171	0.020	1.671	−0.178	0.010
	C_{4v}	−1132.144	0.000	404.27	0.917	0.354	0.068	2.672	0.810	0.123

[a] In hartrees. [b] In atomic units (au). [c] In electronvolts (eV). [d] Geometrical constraints: ∠1−2−4 = ∠3−2−4 = 120.0°. [e] Geometrical constraint: 1−2 = 2.50 Å.

TABLE 4: Energy (E), Relative Energy (E_R), Polarizability (α), Hardness (η), Chemical Potential (μ), and the Electrophilicity (ω) Values of Different Isomers of KAl_4^-

KAl_4^- cluster					Koopmans^c			ΔSCF^c		
Al_4^{2-}	KAl_4^-	E^a	$E_R{}^a$	α^b	η	μ	ω	η	μ	ω
$D_{\infty h}$	$C_{\infty v}$	−1569.696	0.081	922.94	0.259	−0.053	0.005	1.090	−0.181	0.015
C_{3h}	C_{2v} 1^d	−1569.713	0.064	824.49	0.380	0.029	0.001	1.238	−0.151	0.009
	C_{2v} 2^{d,e}	−1569.710	0.059	613.90	0.435	0.156	0.028	1.404	−0.157	0.009
$D_{2h}{}^e$	C_s 1	−1569.758	0.019	637.75	0.531	0.065	0.004	1.399	−0.195	0.014
	C_s 2^f	−1569.740	0.037	622.92	0.418	0.183	0.040	1.205	−0.128	0.007
D_{4h}	C_{2v}	−1569.768	0.009	574.81	0.573	0.140	0.017	1.438	−0.201	0.014
	C_{4v}	−1569.777	0.000	471.43	0.739	0.269	0.049	1.545	−0.164	0.009

[a] In hartrees. [b] In atomic units (au). [c] In electronvolts (eV). [d] Geometrical constraints: ∠1−2−4 = ∠3−2−4 = 120.0°. [e] Geometrical constraint: ∠1−2−3−4 = 0.0°. [f] Geometrical constraint: 1−2 = 2.50 Å.

TABLE 5: Energy (E), Relative Energy (E_R), Polarizability (α), Hardness (η), Chemical Potential (μ), and the Electrophilicity (ω) Values of Different Isomers of $CuAl_4^-$

$CuAl_4^-$ cluster					Koopmans^c			ΔSCF^c		
Al_4^{2-}	$CuAl_4^-$	E^a	$E_R{}^a$	α^b	η	μ	ω	η	μ	ω
$D_{\infty h}$	$C_{\infty v}$	−2610.285	0.086	500.60	0.560	−0.089	0.007	1.662	−0.122	0.005
$C_{3h}{}^d$	C_{2v} 1	−2610.306	0.065	448.85	0.656	0.065	0.003	2.872	−0.422	0.031
	C_{2v} 2	−2610.323	0.048	380.32	0.611	0.016	2E−04	2.198	0.216	0.011
D_{2h}	C_s 1	−2610.326	0.045	396.05	0.409	−0.121	0.018	1.886	−0.450	0.054
	C_s 2^e	−2610.347	0.025	334.64	0.577	−0.035	0.001	1.875	−0.139	0.005
D_{4h}	C_{2v}	−2610.363	0.009	343.96	1.018	0.237	0.028	2.370	0.145	0.004
	C_{4v}	−2610.371	0.000	331.24	0.999	0.291	0.042	2.933	−0.426	0.031

[a] In hartrees. [b] In atomic units (au). [c] In electronvolts (eV). [d] Geometrical constraints: ∠1−2−4 = ∠3−2−4 = 120.0°. [e] Geometrical constraint 1−2 = 2.50 Å.

TABLE 6: Reaction Energies (E_{R*}) of the Reaction Producing MAl_4^- Isomers^a

reaction with Al_4^{2-} (D_{4h}) $M^+ + Al_4^{2-} \rightarrow MAl_4^-$ ^{a}	product	reactant energy^b $E_R = E_{M^+} + E_{Al_4^{2-}}$	product energy^b $E_P = E_{MAl_4^-}$	reaction energy^b $E_{R*} = E_P - E_R$
$Li^+ + Al_4^{2-} \rightarrow LiAl_4^-$	C_{2v}	−977.025	−977.357	−0.331164
	C_{4v}	−977.025	−977.362	−0.336355
$Na^+ + Al_4^{2-} \rightarrow NaAl_4^-$	C_{2v}	−1131.83	−1132.13	−0.306727
	C_{4v}	−1131.83	−1132.14	−0.315900
$K^+ + Al_4^{2-} \rightarrow KAl_4^-$	C_{2v}	−1569.50	−1569.77	−0.266690
	C_{4v}	−1569.50	−1569.78	−0.275576
$Cu^+ + Al_4^{2-} \rightarrow CuAl_4^-$	C_{2v}	−2609.92	−2610.36	−0.445191
	C_{4v}	−2609.92	−2610.37	−0.453965

[a] M = Li, Na, K, and Cu. [b] In hartrees.

$(M_i)C_s$) are stable, although the Al_4^{2-} unit in it with D_{2h} symmetry is unstable. In all the MAl_4^- cases, C_{2v} and C_{4v} structures are stable and the minimum energy structures are of C_{4v} symmetry with the D_{4h} Al_4^{2-} unit intact, as shown by Li et al.[6] Minimum energy structures correspond to the minimum polarizability and maximum hardness in all cases (only the Koopmans approximation gives a slightly harder C_{2v} $CuAl_4^-$ isomer than that of the C_{4v} counterpart, but ΔSCF provides the correct result in all cases), as expected from the MPP and the MHP.

The reaction energies with C_{4v} symmetry are less than those with C_{2v} symmetry for all MAl_4^- compounds, confirming the larger stability of the former. The order of reaction energies is $CuAl_4^- < LiAl_4^- < NaAl_4^- < KAl_4^-$ (both C_{2v} and C_{4v}), prescribing the greater complexation power of alkali metals which increases with an increase in size and electropositive nature. Although the NICS values suggest that both C_{4v} and C_{2v} symmetric MAl_4^- complexes are aromatic in nature, the C_{2v} molecules are more aromatic (NICS value is less negative) than their C_{4v} counterparts.

To understand the aromaticity in these systems better vis-a-vis the minimum energy, minimum polarizability, and maximum hardness criteria, we define three different aromaticity indices, $\Delta X = X_{\text{cyclic}} - X_{\text{open}}$ ($X = E$, α, and η). For cyclic structures,

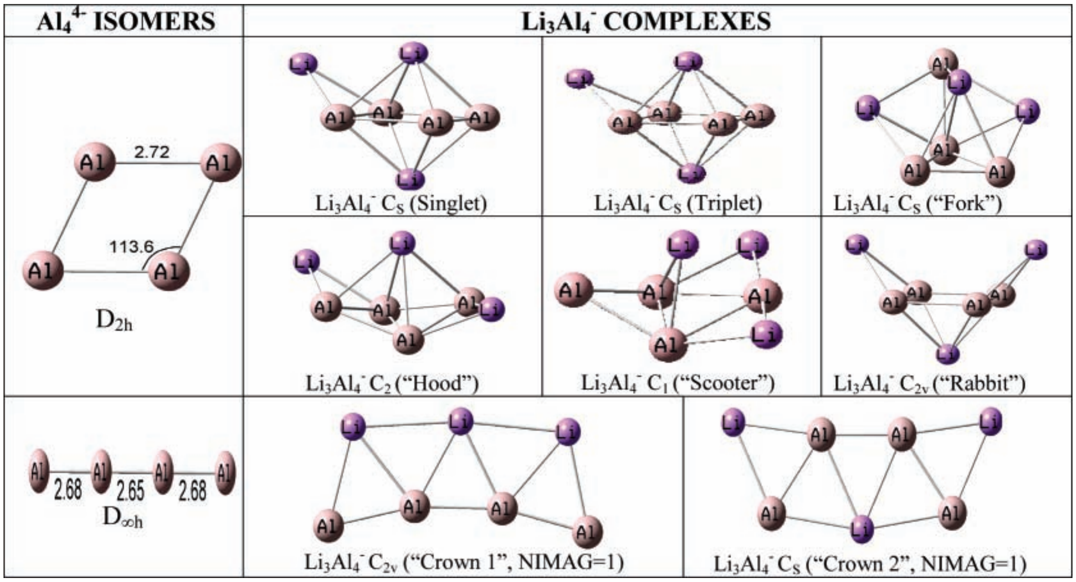


Figure 2. Optimized structures of isomers of Al_4^{4-} and their $Li_3Al_4^-$ complexes.

TABLE 7: Nucleus Independent Chemical Shift (NICS) Values of Al_4^{2-} and its MAl_4^- Complexes[a]

	Al_4^{2-}	$LiAl_4^-$		$NaAl_4^-$		KAl_4^-		$CuAl_4^-$	
	D_{4h}	C_{2v}	C_{4v}	C_{2v}	C_{4v}	C_{2v}	C_{4v}	C_{2v}	C_{4v}
NICS (0)[b]	−34.4166	−35.492	−18.481	−36.673	−24.072	−35.473	−26.875	−38.760	−12.640
NICS (1)[b]	−27.3881	−27.564	−22.712	−28.334	−26.958	−27.536	−25.626	−29.531	−13.403

[a] M = Li, Na, K, and Cu. [b] In parts per million (ppm).

TABLE 8: Relative Energy (Δ*E*), Relative Polarizability (Δα), and Relative Hardness (Δ*η*) Values for Various Isomers of Al_4^{2-}

	cyclic (Al_4^{2-})		open (Al_4^{2-})	$\Delta X = X_{\mathrm{cyclic}} - X_{\mathrm{open}}$[a]	
X[a]	D_{3h}	D_{4h}	$D_{\infty h}$	D_{3h}	D_{4h}
E[b]	−969.7023	−969.7405	−969.6980	−0.004339	−0.04253
α[c]	665.2917	525.7897	675.8190	−10.52733	−150.029
η[d]	1.740756	1.964724	1.511698	0.229058	0.45303

[a] *X* = *E*, α, and *η*. [b] In hartrees. [c] In atomic units (au). [d] In electronvolts (eV) (ΔSCF).

we consider the MAl_4^- system with C_{2v} and C_{4v} structures with the Al_4^{2-} unit with D_{4h} symmetry, and for the linear structures, corresponding $C_{\infty v}$ structures for MAl_4^- ($D_{\infty h}$ for Al_4^{2-}) are taken. *We expect an aromatic system to possess negative* Δ*E and* Δα *values and positive* Δ*η values*. It is worth noting that the Δ*E*, Δα, and Δ*η* values suggest that Al_4^{2-} is aromatic for both D_{4h} and D_{3h} symmetries, and the former isomer is more aromatic (Table 8). All the MAl_4^- systems are aromatic, and as expected, the C_{4v} isomers are more aromatic than the corresponding C_{2v} isomers (Table 9).

All-Metal Antiaromatic Molecule Al_4^{4-} and Its Family. Different isomers of Al_4^{4-} and $Li_3Al_4^-$ with selected geometrical parameters are presented in Figure 2. Tables 10−12 provide the energy, polarizability, hardness, chemical potential, and electrophilicity values of Al_4^{4-} (singlet), Al_4^{4-} (triplet), and Li_4Al_4, respectively. The structures of Li_4Al_4 are shown in Figure 3. It is very important to note that Al_4^{4-} (both singlet and triplet) with a linear structure is energetically slightly more stable than its cyclic counterpart and hence is antiaromatic, as suggested by the corresponding ELF values.[11] However, the Δα and Δ*η* values predict the overall aromatic character for the singlet, as is prescribed by NICS values[12] and magnetic field induced current density values.[13] However, for the triplet, Δα predicts it to be antiaromatic and

TABLE 9: Relative Energy (Δ*E*), Relative Polarizability (Δα), and Relative Hardness (Δ*η*) Values for MAl_4^- Complexes[a]

		cyclic/closed systems with Al_4^{2-} (D_{4h}) isomer			$\Delta X = X_{\mathrm{cyclic}} - X_{\mathrm{open}}$[a]	
X[a]	Al_4^-	MAl_4^- (C_{2v})	MAl_4^- (C_{4v})	open system ($D_{\infty h}$)	C_{2v}	C_{4v}
E[b]	$LiAl_4^-$	−977.3566	−977.3618	−977.2781	−0.078494	−0.0836851
	$NaAl_4^-$	−1132.1350	−1132.1440	−1132.0630	−0.072060	−0.0812325
	KAl_4^-	−1569.7683	−1569.7772	−1569.6961	−0.072186	−0.0810714
	$CuAl_4^-$	−2610.3626	−2610.3714	−2610.2854	−0.077182	−0.0859562
α[c]	$LiAl_4^-$	414.4507	375.031	686.377	−271.926	−311.346
	$NaAl_4^-$	458.2503	404.265	719.792	−261.542	−315.527
	KAl_4^-	574.8107	471.425	922.935	−348.124	−451.510
	$CuAl_4^-$	343.9567	331.2433	500.603	−156.646	−169.360
η[d]	$LiAl_4^-$	1.764831	3.621905	1.273489	0.491342	2.348416
	$NaAl_4^-$	1.670897	2.671846	1.272470	0.398430	1.399374
	KAl_4^-	1.438355	1.545465	1.089918	0.348436	0.455547
	$CuAl_4^-$	2.369911	2.932991	1.661608	0.708303	1.271383

[a] M = Li, Na, K, and Cu; *X* = *E*, α, and *η*. [b] In hartrees. [c] In atomic units (au). [d] In electronvolts (eV) (ΔSCF).

TABLE 10: Energy (*E*), Polarizability (α), Hardness (*η*), Chemical Potential (*μ*), Electrophilicity (*ω*), and the Δ*X*[a] Values of Different Isomers of Al_4^{4-} (Singlet)

			Koopmans[d]			ΔSCF[d]		
Al_4^{4-}	E[b]	α[c]	η	μ	ω	η	μ	ω
D_{2h}	−969.2617	1910.644	0.480	8.796	80.568	1.194	8.703	31.714
$D_{\infty h}$	−969.2664	1915.578	0.241	8.082	135.304	0.954	8.062	34.066

$\Delta E = 0.0047391$, $\Delta\alpha = -4.934333333$, $\Delta\eta = 0.238780035$ (Koopmans); 0.240252172 (ΔSCF)

$\Delta X = X_{D_{2h}} - X_{D_{\infty h}}$[a]

[a] $X = E$, α, and η. [b] In hartrees. [c] In atomic units (au). [d] In electronvolts (eV).

TABLE 11: Energy (*E*), Polarizability (α), Hardness (*η*), Chemical Potential (*μ*), Electrophilicity (*ω*), and the Δ*X*[a] Values of Different Isomers of Al_4^{4-} (Triplet)

			Koopmans[d]			ΔSCF[d]		
Al_4^{4-}	E[b]	α[c]	η	μ	ω	η	μ	ω
D_{2h}	−969.2592	2276.3937	0.5956	8.540	69.982	1.206	8.719	31.521
$D_{\infty h}$	−969.2750	2149.0253	0.4238	7.953	76.984	1.187	8.055	27.321

$\Delta E = 0.0158$, $\Delta\alpha = 127.3684$, $\Delta\eta = 0.1718$ (Koopmans); 0.019 (ΔSCF)

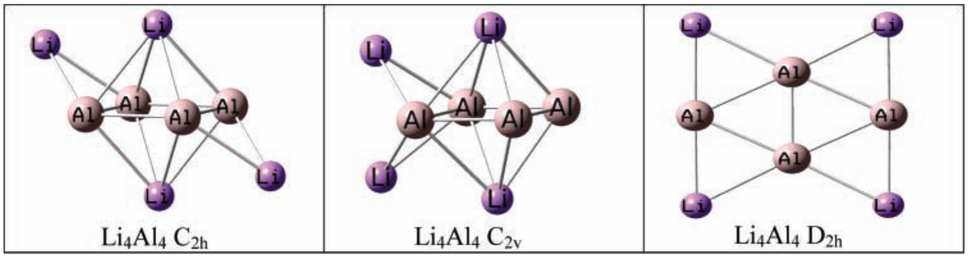
$\Delta X = X_{D_{2h}} - X_{D_{\infty h}}$[a]

[a] $X = E$, α, and η. [b] In hartrees. [c] In atomic units (au). [d] In electronvolts (eV).

TABLE 12: Energy (*E*), Polarizability (α), Hardness (*η*), Chemical Potential (*μ*) and the Electrophilicity (*ω*) Values of the Different Isomers of Li_4Al_4

				Koopmans[d]			ΔSCF[d]		
Li_4Al_4	E[a]	NICS (0)[b]	α[c]	η	μ	ω	η	μ	ω
C_{2h}	−999.9331	−11.182	392.791	0.7203	−2.786	5.389	1.998	−2.868	2.058
C_{2v}	−999.9138	28.5687	364.974	0.5170	−3.044	8.962	1.822	−3.125	2.679
D_{2h}	−999.9324	−3.6252	452.724	0.7695	−2.469	3.962	1.920	−2.579	1.732

[a] In hartrees. [b] In parts per million (ppm). [c] In atomic units (au). [d] In electronvolts (eV).



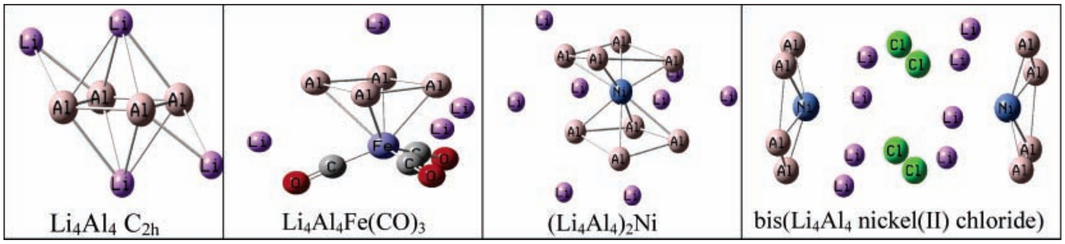
Li_4Al_4 C_{2h} Li_4Al_4 C_{2v} Li_4Al_4 D_{2h}

Figure 3. Optimized structures of isomers of Li_4Al_4.

TABLE 13: Reaction Energies (E_{R*}) of the Reaction Producing Li_4Al_4 Isomers

reaction	product	reactant energy[a] $E_R = E_{Li_4^{4+}} + E_{Al_4^{4-}}$	product energy[a] $E_P = E_{Li_4Al_4}$	reaction energy[a] $E_{R*} = E_P - E_R$
$Li_4^{4+} + Al_4^{4-} \rightarrow Li_4Al_4$	C_{2h}	−998.40136	−999.9331	−1.53174
	C_{2v}	−998.40136	−999.91382	−1.51246
	D_{2h}	−998.40136	−999.93242	−1.53105

[a] In hartrees.



Li_4Al_4 C_{2h} $Li_4Al_4Fe(CO)_3$ $(Li_4Al_4)_2Ni$ bis(Li_4Al_4 nickel(II) chloride)

Figure 4. Optimized structures of Li_4Al_4 and its complexes.

$\Delta\eta$ predicts it to be aromatic. This fact highlights the inadequacy of all these descriptors in unequivocally settling the issue of the aromatic vs antiaromatic nature of Al_4^{4-}. Of course, the ΔE value is so small that it may as well change its sign in other levels of calculation. The aromaticity of Al_4^{2-} is, however, proved by all the descriptors without any confusion. It is transparent that Al_4^{4-} gets stabilized by complexation to form Li_4Al_4 as the energy and polarizability decrease and the hardness increases during the complexation process. Table 13 reports the corresponding reaction energies which show that complexation is a thermodynamically favorable process.

TABLE 14: Energy (E), Relative Energy (E_R), Polarizability (α), Hardness (η), Chemical Potential (μ), and the Electrophilicity (ω) Values of Different Isomers of $Li_3Al_4^-$

$Li_3Al_4^-$ cluster					Koopmans[c]			ΔSCF[c]		
Al_4^{4-}	$Li_3Al_4^-$	E^a	E_R^a	α^b	η	μ	ω	η	μ	ω
D_{2h}	C_s (singlet)	−992.4335	0.001	564.935	0.603	0.520	0.224	1.388	0.073	0.002
	C_s (triplet)	−992.4339	6E−4	530.666	0.736	0.409	0.137	1.460	0.003	3E−6
	C_s (fork)	−992.4345	0	522.497	0.741	0.381	0.098	1.516	−0.026	2E−4
	C_2 (hood)	−992.4303	0.004	602.844	0.650	0.495	0.188	1.393	0.046	8E−4
	C_1(scooter)	−992.4308	0.004	618.850	0.618	0.478	0.185	1.356	0.062	0.001
	C_{2v} (rabbit)	−992.4194	0.015	726.708	0.577	0.417	0.151	1.439	0.161	0.009
$D_{\infty h}$	C_{2v} (crown)	−992.3828	0.052	716.297	0.622	−0.082	0.005	1.627	−0.162	0.008
	C_s (crown)	−992.4045	0.030	720.726	0.668	0.087	0.006	1.513	−0.135	0.006

[a] In hartrees. [b] In atomic units (au). [c] In electronvolts (eV).

TABLE 15: Reaction Energies (E_{R^*}) of the Reaction Producing $Li_3Al_4^-$ Isomers

reaction	product	reactant energy[a] $E_R = E_{Li_3^{3+}} + E_{Al_4^{4-}}$	product energy[a] $E_P = E_{Li_3Al_4^-}$	reaction energy[a] $E_{R^*} = E_P - E_R$
$Li_3^{3+} + Al_4^{4-} \rightarrow Li_3Al_4^-$	C_s (singlet)	−991.1164	−992.4335	−1.3170
	C_s (triplet)	−991.1164	−992.4339	−1.3174
	C_s (fork)	−991.1164	−992.4345	−1.3181
	C_2 (hood)	−991.1164	−992.4303	−1.3139
	C_1 (scooter)	−991.1164	−992.4308	−1.3144
	C_{2v} (rabbit)	−991.1164	−992.4194	−1.3030
	C_{2v} (crown)	−991.1164	−992.3828	−1.2664
	C_s (crown)	−991.1164	−992.4045	−1.2881

[a] In hartrees.

TABLE 16: Nucleus Independent Chemical Shift (NICS) Values of Al_4^{4-} and Its Li_4Al_4 and $Li_3Al_4^-$ Complexes

			$Li_3Al_4^-$					
						at cage		
	Al_4^{4-} D_{2h}	Li_4Al_4 C_{2h}	C_s (singlet)	C_s (triplet)	C_{2v} (rabbit)	C_s (fork)	C_2 (hood)	C_1 (scooter)
NICS (0)[a]	−5.711	−11.182	−5.419	−29.110	−7.0845	−6.1501	−13.2378	−15.2067
NICS (1)[a]	−12.058	1.526	7.809	−20.458	−11.9074			

[a] In parts per million (ppm).

TABLE 17: Energy (E), Polarizability (α), Hardness (η), Chemical Potential (μ), Electrophilicity (ω), and the $\Delta\alpha^{1/3}$ Values of the Li_4Al_4 Isomer and Its Complexes

			Koopmans[d]		
Li_4Al_4 complexes[a]	E^b	α^c	η	μ	ω
Li_4Al_4	−999.932	389.352	0.720699	−2.78660	5.38724
$Li_4Al_4Fe(CO)_3$	−2603.863	370.024	1.167650	−3.25832	4.54615
$(Li_4Al_4)_2Ni$	−3508.302	844.603	0.705869	−2.64225	4.94530
bis(Li_4Al_4 nickel(II) chloride)	−6857.962	660.017	0.783286	−3.71125	8.79207

$$\underset{389.352}{\mathrm{Li_4Al_4}} + \underset{69.6083}{\mathrm{Fe(CO)_3}} \rightarrow \underset{370.024}{\mathrm{Li_4Al_4Fe(CO)_3}} \qquad \Delta\alpha^{1/3} = -4.236469017 \quad (1)$$

$$\underset{389.352}{\mathrm{2Li_4Al_4}} + \underset{1.994}{\mathrm{Ni}} \rightarrow \underset{844.603}{\mathrm{(Li_4Al_4)_2Ni}} \qquad \Delta\alpha^{1/3} = -6.410258433 \quad (2)$$

$$\underset{389.352}{\mathrm{2Li_4Al_4}} + \underset{1.2913}{\mathrm{2Ni^{2+}}} + \underset{5.121}{\mathrm{4Cl^-}} \rightarrow \underset{660.017}{\mathrm{bis(Al_4Li_4\ nickel(II)\ chloride)}} \qquad \Delta\alpha^{1/3} = -14.97007265 \quad (3)$$

[a] Single-point calculation with the geometries and basis in ref 19. [b] In hartrees. [c] In atomic units (au). [d] In electronvolts (eV).

TABLE 18: Reaction Energies (E_R*) of the Reaction Producing the Various Complexes of the Li_4Al_4 Isomer

reaction	reactant energy[a] (E_R)	product energy[a] (E_P)	reaction energy[a] $E_{R^*} = E_P - E_R$
$Li_4Al_4 + Fe(CO)_3 \rightarrow Li_4Al_4Fe(CO)_3$	−2603.682 064	−2603.863 147	−0.181 0832
$2Li_4Al_4 + Ni \rightarrow (Li_4Al_4)_2Ni$	−3507.980 983	−3508.301 692	−0.320 7089
$2Li_4Al_4 + 2Ni^{2+} + 4Cl^- \rightarrow$ bis(Al_4Li_4 nickel(II) chloride)	−6855.359 727	−6857.961 870	−2.602 1428

[a] In hartrees.

Among all the $Li_3Al_4^-$ isomers, the C_s ("fork") structure is the most stable (Table 14), as shown by Li et al.[9] in their DFT calculation. The minimum energy fork structure is the hardest and the least polarizable, as expected from the MHP and the MPP. In this case, Koopmans' and ΔSCF calculations also provide qualitatively different results, owing to the inherent inadequacies of the Koopmans theorem. All the stable structures of $Li_3Al_4^-$ possess lower energy, greater hardness, and smaller polarizability values when compared to those of Al_4^{4-}. Reaction energies for the reaction $Li_3^{3+} + Al_4^{4-} \rightarrow Li_3Al_4^-$ are provided in Table 15. All the reactions are thermodynamically favorable, and the fork product is the most stable. Note, however, that the NICS (0) and NICS (1) values (Table 16) suggest that the C_s (triplet) is the most aromatic. The Al_4^{4-} is overall aromatic (doubly σ-aromatic and singly π-antiaromatic[12]), as shown by others.[13,19] It becomes more aromatic on complexation, but for the C_s (singlet) structure of $Li_3Al_4^-$. Two crown-like structures (NIMAG = 1) and one rabbit-like structure (NIMAG = 0) of $Li_3Al_4^-$ are also shown,[9] all of which are more stable than Al_4^{4-} (considering E, α, η, and the reaction energy values). The capped octahedral singlet isomer is the most stable[9] at the CCSD(T) level of theory.

As in the case of the classic organic antiaromatic molecule cyclobutadiene, stable transition-metal complexes of the all-metal antiaromatic molecule Li_4Al_4 were reported recently,[19] even though there was a confusion regarding its antiaromatic nature.[30] We perform single-point calculations with the geometries and basis sets prescribed in ref 19 for $Li_4Al_4Fe(CO)_3$, $(Li_4Al_4)_2Ni$, and bis(Li_4Al_4 nickel(II) chloride). Figure 4 depicts their optimized structures. For comparison, the Li_4Al_4 (C_{2h}) structure is also included. Table 17 presents the corresponding E, α, η, μ, and ω values. The energy is less and the hardness is more in all complexes in comparison to the corresponding values for Li_4Al_4, but for $(Li_4Al_4)_2Ni$, the η is comparable (slightly less) to the η of Li_4Al_4. Therefore, the complexation stabilizes Li_4Al_4. However, the polarizability values do not decrease during complexation. This may be due to the fact that there is more than one reactant. In this situation, Ghanty and Ghosh [29] have prescribed that the average cube root of the polarizability of the products should be less than that of the reactants, according to the MPP. Those values are provided at the bottom of Table 17. It is important to note that the MPP is obeyed in all three cases. Corresponding reaction energies (Table 18) corroborate this result. A decrease in the NICS value (more negative) on complexation implies[19] more aromaticity. In general, the most stable isomers for the antiaromatic class do not obey the MHP and the MPP.

Chemical potential and electrophilicity behavior in all the systems may be summarized as follows. Wherever μ is positive, the system does not want to take any electrons. However, this behavior is not always reflected through the ω values. Two possible reasons may be the quadratic appearance of μ (or χ) in the definition of ω (although large μ or large χ qualitatively predict opposite behavior, with this definition both will produce large ω) and the relative variations in μ (or χ) and η. Corresponding analysis using various local reactivity descriptors is currently underway in our laboratory.

In case the second point does not create a problem, the large negative μ values go along with large ω values, as expected. This shows the inadequacy of μ and ω in predicting aromaticity in a general sense.

Conclusions

In conclusion, the maximum hardness principle and the minimum polarizability principle can adequately describe the stability and reactivity of all-metal aromatic and antiaromatic compounds such as Al_4^{2-} and Al_4^{4-}, respectively, and their various alkali- and transition-metal complexes. Although an overall aromaticity of Al_4^{4-} is prescribed by most of the aromaticity descriptors, it is puzzling to note that the linear Al_4^{4-} is energetically slightly more stable than its cyclic counterpart (the triplet state polarizability is also less). Two different aromaticity indices are proposed in light of the various electronic structure principles which successfully complement other known criteria of aromaticity based on energetics and magnetic behavior.

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