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Electron Affinities of Al_n Clusters and Multiple-Fold Aromaticity of the Square Al_4^{2-} Structure

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Abstract: The concept of aromaticity was first invented to account for the unusual stability of planar organic molecules with $4n + 2$ delocalized π electrons. Recent photoelectron spectroscopy experiments on all-metal MAl_4^- systems with an approximate square planar Al_4^{2-} unit and an alkali metal led to the suggestion that Al_4^{2-} is aromatic. The square Al_4^{2-} structure was recognized as the prototype of a new family of aromatic molecules. High-level ab initio calculations based on extrapolating CCSD(T)/aug-cc-pVxZ (x = D, T, and Q) to the complete basis set limit were used to calculate the first electron affinities of Al_n, $n = 0-4$. The calculated electron affinities, 0.41 eV ($n = 0$), 1.51 eV ($n = 1$), 1.89 eV ($n = 3$), and 2.18 eV ($n = 4$), are all in excellent agreement with available experimental data. On the basis of the high-level ab initio quantum chemical calculations, we can estimate the resonance energy and show that it is quite large, large enough to stabilize Al_4^{2-} with respect to Al_4. Analysis of the calculated results shows that the aromaticity of Al_4^{2-} is unusual and different from that of C_6H_6. Particularly, compared to the usual (1-fold) π aromaticity in C_6H_6, which may be represented by two Kekulé structures sharing a common σ bond framework, the square Al_4^{2-} structure has an unusual "multiple-fold" aromaticity determined by three independent delocalized (π and σ) bonding systems, each of which satisfies the $4n + 2$ electron counting rule, leading to a total of $4 \times 4 \times 4 = 64$ potential resonating Kekulé-like structures without a common σ frame. We also discuss the 2-fold aromaticity (π plus σ) of the Al_3^- anion, which can be represented by $3 \times 3 = 9$ potential resonating Kekulé-like structures, each with two localized chemical bonds. These results lead us to suggest a general approach (applicable to both organic and inorganic molecules) for examining delocalized chemical bonding. The possible electronic contribution to the aromaticity of a molecule should not be limited to only one particular delocalized bonding system satisfying a certain electron counting rule of aromaticity. More than one independent delocalized bonding system can simultaneously satisfy the electron counting rule of aromaticity, and therefore, a molecular structure could have multiple-fold aromaticity.

Introduction

The concept of aromaticity was developed to explain the unusual stability of planar organic molecules with $4n + 2$ delocalized π electrons.[1,2] This concept has recently been extended and used to interpret the unusual stability of the all-metal structural unit Al_4^{2-} by Li et al.[3] Li et al.'s evidence for the aromatic character of all-metal molecules is that a series of bimetallic clusters with chemical composition MAl_4^- (M = Li, Na, or Cu) possess a pyramidal structure containing an M^+ cation interacting with a square Al_4^{2-} unit having two delocalized π electrons in the highest occupied molecular orbital (HOMO). In addition, the $4n + 2$ electron counting rule is satisfied with the two delocalized π electrons ($n = 0$), and thus the square Al_4^{2-} was proposed to be aromatic.[3] The aromaticity of the square planar Al_4^{2-} structure was rationalized as follows: "Analogy can be made with the prototypical aromatic system, benzene (C_6H_6), in which aromaticity is responsible for its perfect hexagonal structure with all equal C−C bonds, rather than the classical alternating single and double bonds".[3] Experimental and computational studies on analogues to Al_4^{2-} and related aromatic all-metal molecules have also been reported, and the square Al_4^{2-} structure can be considered to be a prototype of a new class of aromatic molecules.[4−8]

High-level ab initio molecular orbital theory calculations of the electron affinities of Al_n clusters for $n = 1-4$ show excellent agreement with the available experimental results. On the basis

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of the high-level ab initio quantum chemical calculations, we can calculate the resonance energy, and use this value to demonstrate how the aromaticity of Al_4^{2-} is unusual and remarkably different from that of C_6H_6. In particular, compared to the usual (1-fold defined) π aromaticity in C_6H_6, which may be represented by two Kekulé structures sharing a common σ frame, the square Al_4^{2-} structure has an unusual "multiple-fold" aromaticity determined by three independent delocalized (π and σ) bonding systems. Each of these delocalized systems satisfies the $4n + 2$ electron counting rule, giving a total of $4 \times 4 \times 4 = 64$ potential resonating Kekulé-like structures without an underlying σ bonding framework.

Computational Approach

We have been developing an approach[9] to the reliable calculation of molecular thermodynamic properties, notably heats of formation, based on ab initio molecular orbital theory. This approach is based on using coupled cluster theory with a perturbative triples correction (CCSD(T))[10−12] with the correlation-consistent basis sets[13,14] extrapolated to the complete basis set limit and then including a number of smaller corrections including core−valence interactions and relativistic effects. For the present study, we used the augmented correlation-consistent basis sets aug-cc-pVxZ for Al (x = D, T, and Q).[15] Only the spherical components (5-d, 7-f, 9-g, and 11-h) of the Cartesian basis functions were used. All of the current work was performed with the MOLPRO suite of programs.[16] The open-shell CCSD(T) calculations were carried out at the R/UCCSD(T) level, where a restricted open-shell Hartree−Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled cluster calculation.[17−19] The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed-exponential/Gaussian function of the form

$$E(n) = E_{\mathrm{CBS}} + A \exp[-(n-1)] + B \exp[-(n-1)^2] \qquad (1)$$

where n = 2 (DZ), 3 (TZ), and 4(QZ), as first proposed by Peterson et al.[20] This extrapolation method has been shown to be the most appropriate method for extrapolations up through $n = 4$. The geometries were optimized at the frozen core CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ levels of theory. The CCSD(T)/aug-cc-pVTZ geometries were used for the CCSD(T)/aug-cc-pVQZ calculations. Vibrational frequencies were calculated at the B3LYP/6-311+G* level on the basis of the B3LYP/6-311+G* geometries.[21,22] All of the calculations were performed on SGI Origin2000 computers.

Core−valence corrections (ΔE_{CV}) were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[23] Scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI-SD (configuration interaction singles and doubles) level of theory using the cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass-velocity and one-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[24]

Various criteria, such as energetic, structural, and magnetic criteria, have been used in the literature[2,25−28] to determine the presence of aromaticity. The energetic criterion, i.e., resonance energy (RE) or aromatic stabilization energy (ASE), is directly related to the stability of the molecular structure. RE (or ASE) is the extra stabilization energy relative to that of a model structure where resonance is not present. It is, of course, difficult to calculate the RE precisely because of the difficulty in defining the model system. The RE value of C_6H_6, the prototypical aromatic molecule, has been determined to be 20 kcal/mol on the basis of Dewar's definition of RE,[2,29] although in the older literature, it is often given as 30−36 kcal/mol on the basis of different approaches.[30] The RE value of 20 kcal/mol was found as the difference between the atomization enthalpy of the conjugated system in C_6H_6 and that of the classical Kekulé reference structure, which has three C═C double bonds and three C−C single bonds. The RE value thus determined is also called the Dewar resonance energy (DRE).[2,29] To make the comparison with C_6H_6 plausible, we have followed Dewar's general approach to calculate the RE value of Al_4^{2-}.

To determine the RE of Al_4^{2-}, we need to know the number of bonding electron pairs in Al_4^{2-}, denoted by $m(Al_4^{2-})$, the reference bond energy of a localized Al−Al single bond, denoted by BE(Al−Al), and the total bond energy of Al_4^{2-}. The total bond energy, i.e., the atomization enthalpy, of Al_4^{2-} can be considered to be the atomization enthalpy change from Al_4^{2-} to 4Al + 2e, denoted by $\Delta E(Al_4^{2-} \rightarrow 4Al + 2e)$. If there is no resonance stabilization, $m(Al_4^{2-})$ pairs of bonding electrons would be expected to form $m(Al_4^{2-})$ localized Al−Al single bonds, giving a total bond energy of $m(Al_4^{2-})$ BE(Al−Al). Thus, the resonance energy of Al_4^{2-}, i.e., $RE(Al_4^{2-})$, may be evaluated through

$$\mathrm{RE}(\mathrm{Al}_4^{\,2-}) = \Delta E(\mathrm{Al}_4^{\,2-} \rightarrow 4\mathrm{Al} + 2\mathrm{e}) - m(\mathrm{Al}_4^{\,2-})\,\mathrm{BE}(\mathrm{Al{-}Al}) \quad (2)$$

To determine $m(Al_4^{2-})$, consider that the Al atom existing in planar aluminum clusters is monovalent. Al only uses its 3p orbital for bonding with other Al atom(s); the 3s orbital remains a core lone pair because the 3s and 3p orbitals are separated by a large energy gap of 4.99 eV.[31] This feature is consistent with recent analyses of the molecular orbitals (MOs) in Al_4^{2-}.[7,8] Each Al atom contributes one bonding electron to Al_4^{2-}, and thus, Al_4^{2-} has a total of six bonding electrons, leading to

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Table 1. Geometric Parameters (Å and deg) Optimized for Al$_n$ and Al$_n^-$ (n = 2−4) and for Al$_4^{2-}$ [a]

method	Al$_2$($^3\Pi_u$)	Al$_2$($^3\Sigma_g^-$)	Al$_2$($^1\Sigma_g^+$)	Al$_2^-$($^4\Sigma_g^-$)	Al$_2^-$($^2\Pi_u$)π^3	Al$_2^-$($^2\Pi_u$)$\sigma^2\pi^1$
B3LYP/6-311+G*	2.762	2.508	3.054	2.585	2.460	
CCSD(T)/aug-cc-pVDZ	2.766	2.537	3.024	2.607	2.517	2.766
CCSD(T)/aug-cc-pVTZ	2.728	2.497	2.976	2.571	2.475	2.732

method	Al$_3$($^2A_1'$)	Al$_3$($^2A_2''$)	Al$_3$($^4A_2$)	Al$_3^-$($^1A_1'$)	Al$_3^-$($^3B_2$)	Al$_3^-$($^3A_2$)
B3LYP/6-311+G*	2.537	2.641	2.605,[b] 3.033 71.19	2.538	2.530,[b] 2.757 66.02	2.604,[b] 2.970 69.54
CCSD(T)/aug-cc-pVDZ	2.591	2.684	2.647,[b] 3.030 69.84	2.585	2.578,[b] 2.792 65.58	2.636,[b] 2.981 68.88
CCSD(T)/aug-cc-pVTZ	2.544	2.636	2.603,[b] 2.948 68.98	2.544	2.537,[b] 2.736 65.26	2.598,[b] 2.923 68.45

method	Al$_4$($^3B_{3g}$)	Al$_4$($^3B_{3u}$)	Al$_4$(^1A_g)	Al$_4$($^3A_{1u}$)
B3LYP/6-311+G*	2.581 111.02, 68.98	2.657 99.92, 80.08	2.495, 2.686 113.85, 66.15	2.668
CCSD(T)/aug-cc-pVDZ	2.617 111.57, 68.43	2.683 102.93, 77.07	2.536, 2.732 113.63, 66.37	2.702
CCSD(T)/aug-cc-pVTZ	2.579 112.12, 67.88	2.639 103.78, 76.22	2.501, 2.676 114.72, 65.28	2.663

method	Al$_4^-$(^2A_g)	Al$_4^-$($^2B_{2g}$)	Al$_4^-$($^2A_{2u}$)	Al$_4^{2-}$($^1A_{1g}$)
B3LYP/6-311+G*	2.568 104.32, 75.68	2.580	2.634	2.592
CCSD(T)/aug-cc-pVDZ	2.604 106.46, 73.54	2.622	2.673	2.639
CCSD(T)/aug-cc-pVTZ	2.566 106.98, 73.02	2.586	2.626	2.602

[a] Bond distances in angstroms, bond angles in degrees. Bond distances given on the first line, bond angles on the second if needed. For Al$_3$, no bond angle means an equilateral triangle, and for Al$_4$, no angle means a square. [b] There are two equivalent bond distances of this value.

m(Al$_4^{2-}$) = 3. To estimate BE(Al−Al), we first consider a diatomic molecule, Al$_2$. Al$_2$ has a triplet ground electronic state ($^3\Pi_u$) with a valence electronic configuration of $1\sigma_g^2 1\sigma_u^2 2\sigma_g^1 1\pi_u^1$.[32] The $1\sigma_g$ and $1\sigma_u$ orbitals are the bonding and antibonding σ MOs, respectively, formed from the 3s atomic orbitals. The $2\sigma_g$ and $1\pi_u$ orbitals are the bonding σ and π MOs, respectively, formed from the 3p orbitals. The triplet ground electronic state of Al$_2$ thus has one singly occupied σ bonding orbital and one singly occupied π bonding orbital. The strength of the two singly occupied Al−Al σ and π bonds should be stronger than that of a doubly occupied Al−Al bond, due to the effect of the electron exchange in the triplet state. So, we expect BE(Al−Al) < ΔE(Al$_2$($^3\Pi_u$) → 2Al). For the lowest singlet state ($^1\Sigma_g$) of Al$_2$, the valence electronic configuration is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$, showing a doubly occupied Al−Al single bond. This doubly occupied Al−Al single bond in the lowest singlet state of Al$_2$ may be considered to be a reference Al−Al single bond; i.e., BE(Al−Al) ≈ ΔE(Al$_2$($^1\Sigma_g$) → 2Al). Assuming BE(Al−Al) = ΔE(Al$_2$($^1\Sigma_g$) → 2Al), eq 2 becomes

$$\mathrm{RE}(\mathrm{Al}_4^{2-}) = \Delta E(\mathrm{Al}_4^{2-} \rightarrow 4\mathrm{Al} + 2\mathrm{e}) - 3\Delta E(\mathrm{Al}_2(^1\Sigma_g) \rightarrow 2\mathrm{Al}) \quad (3)$$

On the basis of eq 3, to evaluate RE(Al$_4^{2-}$), we need ΔE(Al$_4^{2-}$ → 4Al + 2e) and ΔE(Al$_2$($^1\Sigma_g$) → 2Al). These values can be calculated from our extrapolated total energies as described above.

Results and Discussion

The optimized geometry results are shown in Table 1, and the vibrational frequencies are shown in Table 2. Because of the near degeneracy of the σ and π orbitals in Al clusters, there are a number of low-lying states for many of the neutral and anionic clusters. We explored a number of these states, and the various states that we studied are summarized in Table 3, where the various energy components are given. The relative energies of the states together with the electron affinities are given in Table 4. Appropriate experimental energies are also given in Table 4.

Table 2. Vibrational Frequencies (cm^{-1}) Calculated at the B3LYP/6-311+G* Level for Al$_n$ and Al$_n^-$ (n = 2−4) and for Al$_4^{2-}$

Al$_2$($^3\Pi_u$)	Al$_2$($^3\Sigma_g^-$)	Al$_2$($^1\Sigma_g^+$)	Al$_2^-$($^4\Sigma_g^-$)	Al$_2^-$($^2\Pi_u$)π^3
254	324	210	307	341

Al$_3$($^2A_1'$)	Al$_3$($^2A_2''$)	Al$_3$($^4A_2$)	Al$_3^-$($^1A_1'$)	Al$_3^-$($^3B_2$)	Al$_3^-$($^3A_2$)
342 (a_1') 230 (e')	291 (a_1') 162 (e')	297 (a_1) 124 (a_1) 274 (b_2)	350 (a_1') 233 (e')	338 (a_1) 183 (a_1) 258 (b_2)	298 (a_1) 125 (a_1) 209 (b_2)

Al$_4$($^3B_{3g}$)	Al$_4$($^3B_{3u}$)	Al$_4$(^1A_g)	Al$_4$($^3A_{1u}$)
291 (a_g) 167 (a_g) 316 (b_{3g}) 280 (b_{1u}) 206 (b_{2u}) 57 (b_{3u})	272 (a_g) 92 (a_g) 198 (b_{3g}) 260 (b_{1u}) 234 (b_{2u}) 69 (b_{3u})	315 (a_g) 204 (a_g) 162 (a_g) 68 (a_u) 323 (b_u) 230 (b_u)	264 (a_{1g}) 107 (b_{1g}) 377 (b_{2g}) 44i (b_{2u}) 205 (e_u)

Al$_4^-$(^2A_g)	Al$_4^-$($^2B_{2g}$)	Al$_4^-$($^2A_{2u}$)	Al$_4^{2-}$($^1A_{1g}$)
299 (a_g) 131 (a_g) 229 (b_{3g}) 312 (b_{1u}) 261 (b_{2u}) 81 (b_{3u})	293 (a_{1g}) 102 (b_{1g}) 644 (b_{2g}) 78 (b_{2u}) 251 (e_u)	285 (a_{1g}) 144 (b_{1g}) 298 (b_{2g}) 49 (b_{2u}) 253 (e_u)	294 (a_{1g}) 132 (b_{1g}) 307 (b_{2g}) 115 (b_{2u}) 272 (e_u)

The structures and electronic states of small Al clusters have previously been studied by a number of other research groups.[33−41]

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Table 3. Contributions to the Total Energy (au) for Al_n and Al_n^- ($n = 1-4$) and for Al_4^{2-} and Relative Energies (kcal/mol)

contribution[a]	Al	Al^-	$Al_2(^3\Pi_u)$	$Al_2(^3\Sigma_g^-)$	$Al_2(^1\Sigma_g^+)$
aug-cc-pVDZ	−241.9226554	−241.9360744	−483.8903553	−483.8874647	−483.8782110
aug-cc-pVTZ	−241.9314721	−241.9471113	−483.9137448	−483.9115704	−483.9026780
aug-cc-pVQZ	−241.9337375	−241.9497897	−483.9196175	−483.9179165	−483.9088663
est CBS eq 1[b]	−241.934963	−241.951218	−483.922776	−483.92137076	−483.912201
E_{CV}[c]	−0.2543715	−0.2538356	−0.5086384	−0.5088000	−0.5083062
E_{SR}[d]	−0.4347376	−0.4344676	−0.8693652	−0.8693486	−0.8693462
ΔE_{elec} CBS eq 1		10.20	33.16	32.28	26.53
ΔE_{CV}		−0.34	−0.07	0.04	−0.27
ΔE_{SR}		−0.17	−0.10	−0.06	−0.08
ΔE_{SO}[e]	0.21	−0.21	−0.42	−0.42	−0.42
ΔE_{ZPE}[f]			−0.36	−0.46	−0.30
ΣD_0[g]		9.48	32.21	31.38	25.46
ΔH_f(0 K)	78.23 ± 1.0 (exptl)[h]	68.8	124.2	125.1	131.0

contribution[a]	$Al_2^-(^4\Sigma_g^-)$	$Al_2^-(^2\Pi_u)\pi^3$	$Al_2^-(^2\Pi_u)\sigma^2\pi^1$	$Al_3(^2A_1')$	$Al_3(^2A_2'')$	$Al_3(^4A_2)$
aug-cc-pVDZ	−483.9426679	−483.9202927	−483.9172831	−725.8845327	−725.8791455	−725.8786118
aug-cc-pVTZ	−483.9692607	−483.9486985	−483.9454047	−725.9282487	−725.9207931	−725.9193864
aug-cc-pVQZ	−483.9759099	−483.9558916	−483.9524871	−725.9400750	−725.9320590	−725.9299595
est CBS eq 1[b]	−483.979483	−483.959769	−483.956300	−725.946554	−725.938231	−725.935693
E_{CV}[c]	−0.5079335	−0.5078676	−0.5075292	−0.7627801	−0.7625279	−0.7628007
E_{SR}[d]	−0.8690377	−0.8691075	−0.8689911	−1.3038175	−1.3038384	−1.3038340
ΔE_{elec} CBS eq 1	68.75	56.38	54.20	88.89	83.67	82.08
ΔE_{CV}	−0.51	−0.55	−0.76	−0.21	−0.37	−0.20
ΔE_{SR}	−0.27	−0.27	−0.30	−0.25	−0.23	−0.24
ΔE_{SO}[e]	−0.42	−0.42	−0.42	−0.63	−0.63	−0.63
ΔE_{ZPE}[f]	−0.50	−0.49	−0.5[i]	−1.15	−0.88	−0.99
ΣD_0[g]	67.05	54.65	52.2	86.65	81.56	80.02
ΔH_f(0 K)	89.4	101.8	104.2	148.0	153.1	154.7

contribution[a]	$Al_3^-(^1A_1')$	$Al_3^-(^3B_2)$	$Al_3^-(^3A_2)$	$Al_4(^3B_{3g})$	$Al_4(^3B_{3u})$
aug-cc-pVDZ	−725.9517289	−725.9384104	−725.9329177	−967.8758503	−967.8719840
aug-cc-pVTZ	−725.9977031	−725.9840654	−725.9772850	−967.9353182	−967.9308854
aug-cc-pVQZ	−726.0102267	−725.9960299	−725.9888415	−967.9509812	−967.9463164
est CBS eq 1[b]	−726.017099	−726.002535	−725.995115	−967.959508	−967.954706
E_{CV}[c]	−0.7619767	−0.7621064	−0.7620009	−1.0169111	−1.0168430
E_{SR}[d]	−1.3035142	−1.3034900	−1.3035243	−1.7383844	−1.7383829
ΔE_{elec} CBS eq 1	133.16	124.02	119.37	137.83	134.82
ΔE_{CV}	−0.71	−0.63	−0.70	−0.36	−0.40
ΔE_{SR}	−0.44	−0.43	−0.43	−0.36	−0.36
ΔE_{SO}[e]	−0.63	−0.63	−0.63	−0.84	−0.84
ΔE_{ZPE}[f]	−1.17	−1.11	−0.90	−1.88	−1.61
ΣD_0[g]	130.21	121.22	116.71	134.39	131.61
ΔH_f(0 K)	104.5	113.5	118.0	178.5	181.3

contribution[a]	$Al_4(^1A_g)$	$Al_4(^3A_{1u})$	$Al_4^-(^2A_g)$	$Al_4^-(^2B_{2g})$	$Al_4^-(^2A_{2u})$	$Al_4^{2-}(^1A_{1g})$
aug-cc-pVDZ	−967.8684812	−967.8678116	−967.9519440	−967.9497634	−967.9484868	−967.8946437
aug-cc-pVTZ	−967.9293386	−967.9245350	−968.0151292	−968.0110606	−968.0102269	−967.9586660
aug-cc-pVQZ	−967.9456014	−967.9393243	−968.0318407	−968.0270415	−968.0263758	−967.9757892
est CBS eq 1[b]	−967.954485	−967.947355	−968.040947	−968.035719	−968.035152	−967.985145
E_{CV}[c]	−1.0167783	−1.017463	−1.0161303	−1.0168480	−1.0165206	−1.0154731
E_{SR}[d]	−1.7382524	−1.7386405	−1.7379825	−1.7382845	−1.7381648	−1.7378087
ΔE_{elec} CBS eq 1	134.68	130.21	188.94	185.66	185.30	153.92
ΔE_{CV}	−0.44	−0.01	−0.85	−0.40	−0.60	−1.26
ΔE_{SR}	−0.44	−0.19	−0.61	−0.42	−0.49	−0.72
ΔE_{SO}[e]	−0.84	−0.84	−0.84	−0.84	−0.84	−0.84
ΔE_{ZPE}[f]	−1.86	[j]	−1.88	−2.33	−1.83	−1.99
ΣD_0[g]	131.10		184.76	181.67	181.54	149.11
ΔH_f(0 K)	181.8		128.2	131.2	131.4	163.8

[a] Total energies in hartrees and energy differences in kilocalories per mole. [b] Estimated frozen core, complete basis set energies obtained from eq 1 using the CCSD(T)/aug-cc-pV*x*Z (x = D, T, and Q) energies. [c] Core−valence corrections were obtained from R/UCCSD(T)/cc-CVTZ calculations. [d] Scalar relativistic corrections were obtained from CI/aug-cc-pVTZ MVD calculations. [e] Net spin−orbit correction to the atomization energy from the Al atom. [f] Contributions from the zero-point vibrational energies. [g] $\Sigma D_0 = \Delta E_{elec} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO} + \Delta E_{ZPE}$. [h] Heat of formation of Al at 0 K from Chase, M. W., Jr. NIST-JANAF Tables (4th Edition). *J. Phys. Chem. Ref. Data* **1998**, Monogr. 9, Suppl. 1. [i] Frequency estimated from the value for the $Al_2^-(^2\Pi_u)\pi^3$ state because we were not able to calculate this state at the DFT level. [j] We were unable to optimize the geometry of this state by using the DFT method. See the text for details.

Bauschlicher et al.[34] determined the ground state of Al_2 to be $^3\Pi_u$, consistent with our results. Sunil and Jordan's results[36] indicate that the ground state of Al_2^- anion is $^4\Sigma_g^-$. They also reported two $^2\Pi_u$ states associated with the dominant valence electron configurations π^3 and $\sigma^2\pi^1$, and found that the energy

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Table 4. Calculated Energy Differences in Kilocalories per Mole (and in Electronvolts)

species	EA(calcd)	EA(exptl)
Al	9.48 (0.41)	10.00 (0.4338)[d]
Al_2	34.84 (1.51)	33.67 (1.46),[c] 36.90 (1.60 + 0.10)[b]
Al_3	43.56 (1.89)	43.81 (1.90 + 0.03),[a] 43.81 (1.90 + 0.10)[b]
Al_4	50.37 (2.18)	49.35 (2.14 + 0.04),[e] 50.73 (2.20 + 0.10)[b]

[a] Reference 50. [b] Reference 49. [c] Reference 48. [d] Reference 47. [e] Reference 51.

of the $^2\Pi_u$ state corresponding to π^3 is lower than that corresponding to $\sigma^2\pi^1$. Our results calculated at the CCSD(T) level are all consistent with their conclusions, although we were unable to optimize the geometry of the second $^2\Pi_u$ state corresponding to $\sigma^2\pi^1$ by using the DFT method.

Pettersson, Bauschlicher, and Halicioglu's results[37] at the CCI+Q level indicate that the energy of the lowest doublet state ($^2A_1'$ in an equilateral triangle geometry with D_{3h} symmetry) of Al_3 is very close to that of the lowest quartet state ($^4A_2$ with C_{2v} symmetry); the latter is lower by ~0.01 eV (~0.23 kcal/mol). Our results calculated at a higher level show that the $^2A_1'$ state is the ground state, consistent with the magnetic deflection measurements of Al_3, which indicate a doublet ground state,[42] although the earlier electron spin resonance measurements of matrix-isolated Al_3 indicated a quartet ground state.[43] For the Al_3^- anion, our results clearly indicate that the ground state is singlet, i.e., $^1A_1'$, with D_{3h} symmetry.

For Al_4, Pettersson, Bauschlicher, and Halicioglu's results[37] demonstrated that the planar rhombus structure is lower in energy than the tetrahedral and pyramidal structures, although they calculated only one electronic state ($^3B_{1u}$ with respect to the molecular orientation with the four Al atoms in the *xy* plane) for the planar rhombus structure (D_{2h} symmetry). We examined a total of three possible triplet states ($^3B_{3g}$, $^3B_{3u}$, and ^3A_u) and an additional singlet state (^1A_g) of the planar rhombus structure, and found that the $^3B_{3g}$ state is the lowest in energy. In our calculations on the planar structures with D_{2h} symmetry, the four Al atoms are in the *yz* plane as defined by the "standard orientation" of the Gaussian98 program, instead of the *xy* plane used by Pettersson, Bauschlicher, and Halicioglu, so their $^3B_{1u}$ state corresponds to our $^3B_{3u}$ state. Three states ($^3B_{3g}$, $^3B_{3u}$, and ^1A_g) were found to be associated with local minima on the potential energy surface, whereas the ^3A_u state was found to have D_{4h} symmetry (under D_{4h} symmetry, the state is actually $^3A_{1u}$) associated with a first-order saddle point, evident from the imaginary vibrational frequency given in Table 2. The imaginary vibration mode points to a nonplanar structure having C_{2v} symmetry. The ^3A_u (D_{2h}) or $^3A_{1u}$ (D_{4h}) state becomes a $^3A_2$ state under C_{2v} symmetry. However, we were unable to optimize the geometry of this state by using the DFT method; the geometry optimization under C_{2v} symmetry always went to the planar $^3B_{3g}$ state. This is because both the ^3A_u (D_{2h}) and $^3B_{3g}$ (D_{2h}) states correspond to $^3A_2$ under C_{2v} symmetry (with the consideration of the molecular orientation change); the DFT geometry optimization always went to the lowest $^3A_2$ state. This implies that the $^3A_2$ (C_{2v}) state distorted from the ^3A_u (D_{2h}) or $^3A_{1u}$ (D_{4h}) state should be higher in energy than the $^3B_{3g}$ (D_{2h}) state, consistent with the $^3B_{3g}$ (D_{2h}) state being the ground state. Starting from the ground state ($^1A_{1g}$) of the Al_4^{2-} dianion (D_{4h}), three doublet states of Al_4^- anion can be obtained by removing an electron from each of the three doubly occupied orbitals (a_{1g}, b_{2g}, and a_{2u}). The results listed in Table 3 reveal that the ground state of Al_4^- anion is ^2A_g (D_{2h}) distorted from $^2A_{1g}$ (D_{4h}).

We can compare our calculated ground-state results with the available experimental data. The geometry predicted for Al_2 is 2.728 Å at the CCSD(T)/aug-cc-pVTZ level in comparison with the experimental value of 2.701 ± 0.002 Å from high-resolution spectroscopy measurements.[32] Larger basis sets and including additional core functions will shorten this bond distance by ~0.02 Å.[44] The theoretical $\Delta E(Al_2(^3\Pi_u) \rightarrow 2Al)$ value of 32.21 kca/mol is in excellent agreement with the experimental values of ~31 kcal/mol[45] and 31.8 ± 1.43 kcal/mol.[46] The binding of an aluminum to Al_2 to form Al_3 is exothermic by 54.4 kcal/mol as compared to a value of 32.2 kcal/mol to add Al to Al to form the dimer. Formation of the tetramer by addition of Al to Al_3 releases 47.7 kcal/mol, less energy than to form the trimer from the dimer.

The calculated electron affinities are in excellent agreement with the experimental values considering the size of the error limits on the experimental values, as seen in Table 4. The calculated value for Al is within ~0.5 kcal/mol of the accurate experimental value.[47] For Al_2, the calculated value lies between the two experimental values.[48,49] For Al_3, the calculated value is within 0.5 kcal/mol of the experimental values,[50] and for Al_4, the calculated EA is within 1 kcal/mol of the best experimental value[51] (and within the error bars) and, as for Al_2, lies between the two experimental values.[49] The formation of Al_4^{2-} is exothermic by 14.7 kcal/mol as compared to the asymptote of Al_4 + two electrons, although it is less stable by 35.6 kcal/mol as compared to the asymptote of Al_4^- + an electron. Al_4^{2-} is stable with respect to other asymptotes such as Al_3^- + Al, Al_3 + Al^-, and $2Al_2^-$, as shown from the energies listed in Table 3.

Although our focus is the energy of the ground states relevant to the aromaticity, there are a number of low-lying excited states for the neutrals and the corresponding anions as noted above. For Al_2, the $^3\Sigma_g^-$ state is only 0.83 kcal/mol above the $^3\Pi_u$ ground state followed by the $^1\Sigma_g^+$ state, which is 6.8 kcal/mol above the ground state. For Al_2^-, $^4\Sigma_g^-$ is the ground state and there is a $^2\Pi_u$ excited state formed from the π^3 occupancy, 12.4 kcal/mol above the ground state, with a second $^2\Pi_u$ excited state formed from the $\sigma^2\pi^1$ occupancy estimated to be 14.8 kcal/mol above the ground state. For Al_3, the excited $^2A_2''$ state is 5.1 kcal/mol higher in energy than the $^2A_1'$ ground state and the $^4A_2$ state is 6.6 kcal/mol higher. For Al_3^-, the $^3B_2$ state is 9.0 kcal/mol above the $^1A_1'$ ground state and the $^3A_2$ state is 13.5 kcal/mol higher in energy than the ground state. For Al_4, the state energies are closer, with the $^3B_{3u}$ excited state 2.8 kcal/

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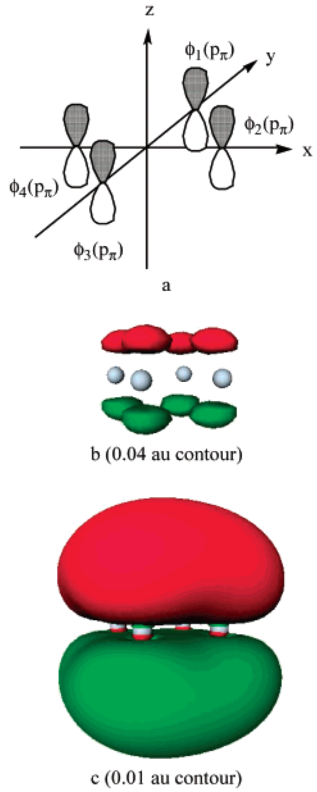
mol higher in energy than the $^3B_{3g}$ ground state, and the ^1A_g state 3.4 kcal/mol higher in energy than the ground state. For Al_4^-, the $^2B_{2g}$ excited state is 3.3 kcal/mol higher than the ^2A_g ground state and the $^2A_{2u}$ state is 3.6 kcal/mol higher in energy than the ground state. The significant number of low-lying neutral and anionic states should lead to very complex photoelectron spectra.

The calculated value for $\Delta E(Al_4^{2-} \rightarrow 4Al + 2e)$ is 149.1 kcal/mol. The dissociation energies for $\Delta E(Al_2(^1\Sigma_g) \rightarrow 2Al)$ and $\Delta E(Al_2(^3\Pi_u) \rightarrow 2Al)$ are 25.5 and 32.2 kcal/mol, respectively. The excellent agreement of the calculated $\Delta E(Al_2(^3\Pi_u) \rightarrow 2Al)$ value with the experimental values of ~31 kcal/mol[45] and 31.8 ± 1.43 kcal/mol[46] further confirms the accuracy of our computational protocol used to predict $\Delta E(Al_4^{2-} \rightarrow 4Al + 2e)$ and $\Delta E(Al_2(^1\Sigma_g) \rightarrow 2Al)$. The predicted $\Delta E(Al_4^{2-} \rightarrow 4Al + 2e)$ and $\Delta E(Al_2(^1\Sigma_g) \rightarrow 2Al)$ values, along with eq 3, lead to $RE(Al_4^{2-}) = 72.7$ kcal/mol. According to our best estimate, the resonance energy of Al_4^{2-} (~73 kcal/mol) is more than 3.6 times of that of C_6H_6 (20 kcal/mol),[2] even though the bond energy of an Al−Al single bond (~26 kcal/mol) is only about one-third of a typical C−C single bond energy (e.g., 89.9 ± 0.5 kcal/mol in CH_3–CH_3[46]).

It should be emphasized that the approach used by Dewar et al.[2,29] to obtain the $RE(C_6H_6)$ value of 20 kcal/mol is consistent with our approach for determining the $RE(Al_4^{2-})$ value of 72.7 kcal/mol. The approach of Dewar et al. is based on the atomization enthalpy difference, so we chose to use the atomization limit $\Delta E(Al_4^{2-} \rightarrow 4Al + 2e)$, rather than the limit $\Delta E(Al_4^{2-} \rightarrow 2Al + 2Al^-)$. If we use the latter limit, the calculated $RE(Al_4^{2-})$ value only decreases to 53.8 kcal/mol. We note that even a value of ~54 kcal/mol is still a significant quantity for the resonance energy. Dewar's resonance energy definition was originally proposed for evaluating the resonance energy of cyclic organic molecules. Such an approach has not been applied to metallic systems whose relative stability can, otherwise, be interpreted in terms of the nonadditive metallic bonds. On the other hand, the nonadditivity of metallic bonds may also be understood, in our point of view, as a result of the electron delocalization in the metallic system. Therefore, it is reasonable for the comparison between the resonance energies of organic C_6H_6 and metallic Al_4^{2-} to use Dewar's general approach of resonance energy. Within Dewar's general approach of resonance energy, our calculated $RE(Al_4^{2-})$ value of 72.7 kcal/mol is based on the assumption that the standard bond energy of a doubly occupied localized Al−Al bond, i.e., BE(Al−Al), is approximately equal to $\Delta E(Al_2(^1\Sigma_g) \rightarrow 2Al)$. We assume $BE(Al-Al) \approx \Delta E(Al_2(^1\Sigma_g) \rightarrow 2Al)$, rather than $BE(Al-Al) \approx \Delta E(Al_2(^3\Pi_u) \rightarrow 2Al)$, because we are studying a delocalized system in which all electrons are paired whereas the larger $\Delta E(Al_2(^3\Pi_u) \rightarrow 2Al)$ value contains the extra contribution from the effect of the electron exchange between the two unpaired electrons in the triplet state. If we assume $BE(Al-Al) \approx \Delta E(Al_2(^3\Pi_u) \rightarrow 2Al)$, the calculated $RE(Al_4^{2-})$ value is 52.5 kcal/mol, which is still more than 2.6 times the $RE(C_6H_6)$ value. The value of 52.5 kcal/mol based on $BE(Al-Al) \approx \Delta E(Al_2(^3\Pi_u) \rightarrow 2Al)$ can be regarded as a lower limit of the $RE(Al_4^{2-})$ value, whereas the value of 72.7 kcal/mol based on $BE(Al-Al) \approx \Delta E(Al_2(^1\Sigma_g) \rightarrow 2Al)$ can be considered to be the upper limit. In either case, the resonance energy of Al_4^{2-} is considerably larger than that of C_6H_6.



a

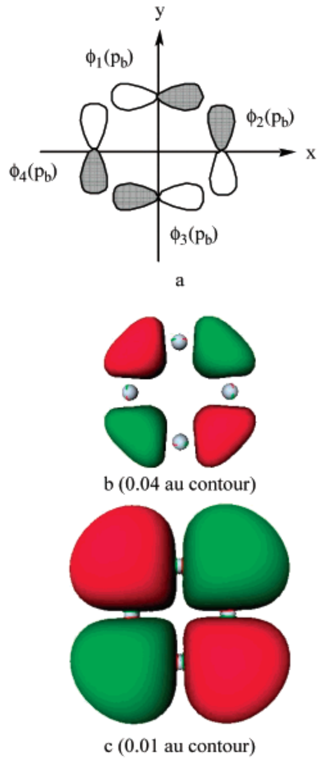
b (0.04 au contour)

c (0.01 au contour)

Figure 1. Delocalized bonding molecular orbital $\psi_1(p_\pi)$: (a) schematic representation; (b) 0.04 au contour; (c) 0.01 au contour.

Why is the resonance energy of Al_4^{2-} so large? This question can be answered by looking into a unique feature of the valence MOs of the square planar Al_4^{2-} structure. An analysis of the MOs calculated for Al_4^{2-} at all levels consistently indicates that each Al atom in the square structure uses two pure p orbitals (denoted by p_π in Figure 1a and p_b in Figure 2a) and two s−p hybrid orbitals to form MOs with the other three Al atoms. One of the two s−p hybrid orbitals has very large s character with little p character and, therefore, can be considered to be an s orbital. The other s−p hybrid orbital has large p character with little s character and can approximately be regarded to be a p orbital, denoted by p_a in Figure 3a for convenience. Because the energy of the s orbital is much lower than that of the p orbital for the Al atom, the s orbital has the lowest energy, and p_b and p_π have the highest energy. Hence, there are four types of valence atomic orbitals (i.e., s, p_a, p_b, and p_π); p_π-type orbitals lead to π MOs out of the plane, and s, p_a, and p_b lead to three types of MOs in the plane. Linear combinations of each type of atomic orbital give four MOs denoted by ψ_1, ψ_2, ψ_3, and ψ_4 in Figure 4; ψ_1 is a bonding MO, ψ_4 is antibonding, and ψ_2 and ψ_3 are nonbonding. The 14 valence electrons of Al_4^{2-} doubly occupy 7 lowest valence MOs: $\psi_1(s)$, $\psi_2(s)$, $\psi_3(s)$, $\psi_4(s)$, $\psi_1(p_b)$, $\psi_1(p_a)$, and $\psi_1(p_\pi)$. They are the HOMO − 5 ($1a_{1g}$), HOMO − 4 ($1e_u$), HOMO − 3 ($1b_{1g}$), HOMO − 2 ($1b_{2g}$), HOMO − 1 or NHOMO ($2a_{1g}$), and HOMO ($1a_{2u}$), respectively, depicted in Figure 3 of ref 3.

The MOs clearly reveal that $\psi_1(s)$, $\psi_2(s)$, $\psi_3(s)$, and $\psi_4(s)$ are linear combinations of the four lone pair atomic orbitals, consistent with a previous analysis.[7] The overall bonding contribution of eight valence electrons occupying the four MOs formed from the s orbitals is approximately zero. The remaining six valence electrons doubly occupy three bonding MOs: $\psi_1(p_a)$,

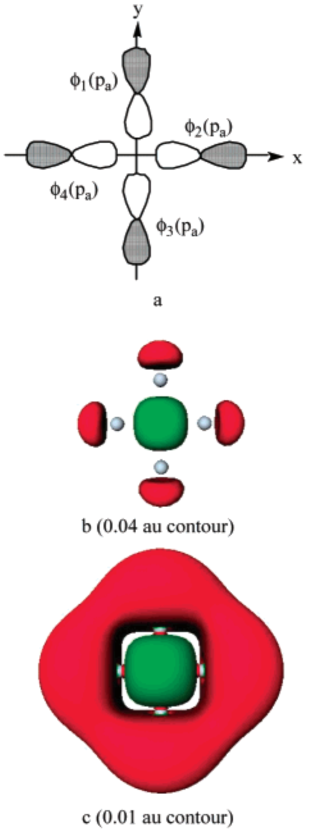


a

b (0.04 au contour)

c (0.01 au contour)

Figure 2. Delocalized bonding molecular orbital $\psi_1(p_b)$: (a) schematic representation; (b) 0.04 au contour; (c) 0.01 au contour.



a

b (0.04 au contour)

c (0.01 au contour)

Figure 3. Delocalized bonding molecular orbital $\psi_1(p_a)$: (a) schematic representation; (b) 0.04 au contour; (c) 0.01 au contour.

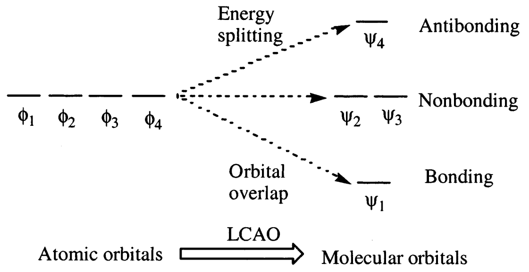


Figure 4. Orbital energy diagram for Al_4^{2-}: $\psi_1 = (\phi_1 + \phi_2 + \phi_3 + \phi_4)/N_1$; $\psi_2 = (\phi_1 + \phi_2 - \phi_3 - \phi_4)/N_2$; $\psi_3 = (\phi_1 - \phi_2 - \phi_3 + \phi_4)/N_3$; $\psi_4 = (\phi_1 - \phi_2 + \phi_3 - \phi_4)/N_4$.

$\psi_1(p_b)$, and $\psi_1(p_\pi)$ formed from p_a, p_b, and p_π, respectively. $\psi_1(p_\pi)$ is a pure π MO, whereas $\psi_1(p_a)$ and $\psi_1(p_b)$ can be regarded as σ MOs as far as the type (i.e., "head-to-head" or "shoulder-to-shoulder" overlap) of the orbital overlaps between the neighboring atoms shown in Figures 1−3 is concerned. Thus, Al_4^{2-} has one delocalized pure π bond and two delocalized σ bonds. The pure π orbital is actually polarized by mixing with d orbitals, although the d character is only 2%. The 0.04 contour of the $\psi_1(p_\pi)$ orbital in Figure 1b seems to suggest more d character in the regions near the atomic nuclei, but this is due to the fact that the Gaussian exponents of the d orbitals are much larger than those of the corresponding p orbitals.

C_6H_6 can be represented by two resonating (covalent) Kekulé structures, ignoring minor contributions from Dewar-type and ionic structures having higher energies.[2] The only difference between these two Kekulé structures is the position of the three π bonds. The σ bonds, including six equal C−C σ bonds and six equal C−H σ bonds, are exactly the same. Compared to C_6H_6, the square planar structure of Al_4^{2-} also has a delocalized π electron system (with only two π electrons but still following the $4n + 2$ rule). However, the chemical bonding in the molecular plane of Al_4^{2-} considerably differs from that of C_6H_6 as Al_4^{2-} does not have a localized "σ framework". To have a localized σ framework like what C_6H_6 has, Al_4^{2-} would need four pairs of σ electrons to form four localized Al−Al σ bonds. There are only six electrons (three pairs) contributing to the chemical bonding in Al_4^{2-}, occupying three delocalized MOs, i.e., $\psi_1(p_a)$, $\psi_1(p_b)$, and $\psi_1(p_\pi)$. As illustrated in Figure 4, each of the three delocalized bonding MOs, i.e., $\psi_1(p_a)$, $\psi_1(p_b)$, and $\psi_1(p_\pi)$, can be expressed as a linear combination of the four atomic orbitals via $\psi_1 = (\phi_1 + \phi_2 + \phi_3 + \phi_4)/N_1$ in which N_1 is a normalization constant. Equivalently, ψ_1 can also be expressed as a linear combination of four localized bonding MOs as

$$\psi_1 = (\psi_{L12} + \psi_{L23} + \psi_{L34} + \psi_{L41})/N_1' \equiv (\phi_1 + \phi_2 + \phi_3 + \phi_4)/N_1 \quad (4)$$

where $\psi_{L12} = (\phi_1 + \phi_2)/N_L$, $\psi_{L23} = (\phi_2 + \phi_3)/N_L$, $\psi_{L34} = (\phi_3 + \phi_4)/N_L$, $\psi_{L41} = (\phi_4 + \phi_1)/N_L$, and N_1' and N_L are the normalization constants. An important implication of eq 4 is that the delocalized chemical bond associated with ψ_1 may be represented by four resonating bonding structures, each with one of the four equivalent localized chemical bonds associated with ψ_{L12}, ψ_{L23}, ψ_{L34}, and ψ_{L41}. Because $\psi_1(p_a)$, $\psi_1(p_b)$, and $\psi_1(p_\pi)$ are orthogonal to each other and are formed from different types of atomic orbitals, each of the three delocalized bonding MOs have four independent resonating bonding structures. Therefore, the complete picture of the chemical bonding in Al_4^{2-} may be represented by a total of 4 × 4 × 4 = 64 potential resonating Kekulé-like structures. The reso-

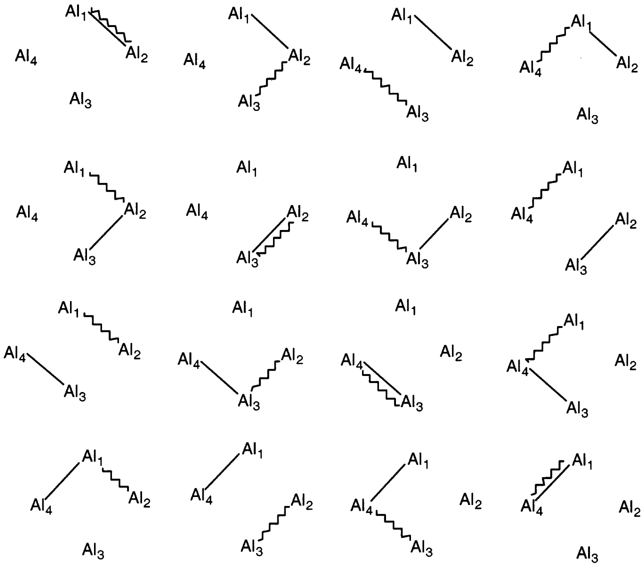


Figure 5. The 16 resonating bonding structures due to the presence of the π bond with a σ bond localized along the line of centers between adjacent Al atoms of Al_4^{2-}. If the third bond (see the text) is included, each of these 16 bonding structures will become 64 potential Kekulé-like structures.

nance structures of Al_4^{2-} can be represented by a two-electron pure π bond associated with a $\psi_1(p_\pi)$ bond, leading to four structures coupled to two sets of two-electron bonds, each of which also has four structures in the molecular plane, leading to $4 \times 4 \times 4 = 64$ resonance structures based on two-electron bonds. The description of resonance structures in Al_n clusters is complicated by the fact that the lowest state for Al_2 is a triplet actually composed of a one-electron σ bond and a one-electron π bond with a triplet state composed of two one-electron π bonds only ~1 kcal/mol higher in energy. The singlet state of Al_2 with a doubly occupied σ bond is ~7 kcal/mol higher than the ground triplet state. The resonating bonding structures due to the presence of the π bond with a σ bond localized along the line of centers between two adjacent Al atoms is shown in Figure 5. If one considers the σ bond between the two atoms to fall on the line between the atomic centers, then the remaining in-plane bond can be considered to be an in-plane π bond like that in acetylene, HCCH. For example, following Figures 2a and 3a, $\psi_{L12}(p_a)$, i.e., $\phi_1(p_a) + \phi_2(p_a)$, and $\psi_{L12}(p_b)$, i.e., $\phi_1(p_b) + \phi_2(p_b)$, are clearly associated with bent, in-plane σ bonds between the two adjacent Al atoms. These orbitals can be transformed by a linear combination of $\psi_{L12}(p_a)$ and $\psi_{L12}(p_b)$ to give a σ bond corresponding to a localized MO, $\sim\psi_{L12}(p_a) - \psi_{L12}(p_b)$, and an in-plane π bond corresponding to a localized MO, $\sim\psi_{L12}(p_a) + \psi_{L12}(p_b)$, between the two adjacent Al atoms. It should be noted that these 64 potential structures are proposed only on the basis of the analysis of the three delocalized molecular orbitals. An accurate generalized valence bond calculation based on these 64 potential Kekulé-like structures will likely lead to different weights for different types of Kekulé-like structures. In particular, the weights for the four structures associated with triple Al−Al bonds are expected to be very small. In any case, the existence of the three independent delocalized bonding systems, each with two electrons satisfying the $4n + 2$ electron counting rule of aromaticity, is unusual, but provides a better understanding of the unusually large resonance energy of Al_4^{2-} and other calculated results reported in the literature. For example, in the discussion of the magnetic criterion of aromaticity, Fowler et al.[52] found that the σ electrons contribute to the delocalized diamagnetic current in Al_4^{2-} induced by a perpendicular magnetic field and Sundholm et al.[4] found that π electrons contribute to the diatropic ring current in Al_4^{2-}. Our analysis provides a better understanding of these calculated results.

The concept of σ aromaticity has been used for hydrocarbons in the literature[2,53,54] for over 25 years. Our concept and the orbital analysis approach of multiple-fold aromaticity is being proposed here for the first time, as far as we are aware. Our general approach for describing the multiple-fold aromaticity of the square Al_4^{2-} structure can be applied to other systems. As an example, we consider Al_3^-, whose π aromaticity was discussed recently by Kuznetsov and Boldyrev.[55] Their theoretical evidence for the aromaticity of Al_3^- includes (1) its cyclic structure, (2) the (obvious) planarity, (3) the presence of $4n + 2$ π electrons, (4) conjugation, (5) the structural integrity of the Al_3^- anion inside the $NaAl_3$ salt, and (6) the electronic integrity of the Al_3^- anion inside the $NaAl_3$ salt.[55] We now describe the multiple-fold aromaticity of Al_3^- on the basis of its calculated wave function and the energetic results listed in Table 3. The MOs calculated for Al_3^- anion in its ground state ($^1A_1'$ for D_{3h} symmetry) show that the four valence electrons are associated with two independent delocalized bonding systems, one π and one σ. Each of the two delocalized bonding systems has one bonding MO and two degenerate antibonding MOs. The four valence electrons doubly occupy a bonding π MO and a bonding σ MO so that the two independent delocalized bonding systems each satisfy the $4n + 2$ counting rule ($n = 0$ for both cases). Further, because each delocalized bonding system is associated with three localized bonding structures, Al_3^- can be represented by a total of $3 \times 3 = 9$ potential resonating Kekulé-like structures, each with two localized chemical bonds. On the basis of this simple analysis, Al_3^- has 2-fold aromaticity. Using the Dewar resonance energy model, following the approach used for $RE(Al_4^{2-})$ (eq 3), we obtain the following for $RE(Al_3^-)$:

$$RE(Al_3^-) = \Delta E(Al_3^- \rightarrow 3Al + e) - 2\Delta E(Al_2(^1\Sigma_g) \rightarrow 2Al) \tag{5}$$

This leads to an upper limit for $RE(Al_3^-)$ of 79.3 kcal/mol. If we use the $\Delta E(Al_2(^3\Pi_u) \rightarrow 2Al)$ dissociation energy, instead of $\Delta E(Al_2(^1\Sigma_g) \rightarrow 2Al)$, $RE(Al_3^-)$ would be 65.8 kcal/mol as a lower limit. If we use the $\Delta E(Al_3^- \rightarrow 2Al + Al^-)$ limit, instead of the $\Delta E(Al_3^- \rightarrow 3Al + e)$ limit, then the above upper and lower limit values of $RE(Al_3^-)$ become 69.8 and 56.3 kcal/mol, respectively. The surprisingly large $RE(Al_3^-)$ value is consistent with the conclusion reached above based on the analysis of the orbitals that 2-fold aromaticity is present. The $RE(Al_4^{2-})$ value associated with 3-fold aromaticity is of the same order of magnitude as that of the corresponding $RE(Al_3^-)$ value associated with 2-fold aromaticity, because the anion is more stable than the dianion for these small clusters where electron repulsion due to the additional negative charge plays an important role.

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Conclusion

From an energetic criterion, in terms of the magnitude of the (Dewar) resonance energy, the aromaticity of the square planar Al_4^{2-} structure is multiple-fold as compared to the usual "1-fold" aromaticity of the well-known C_6H_6 structure. The calculated RE(Al_4^{2-}) value provides a basis for further discussion of the aromaticity of other interesting molecules containing the Al_4^{2-} structural unit and discussion of the complicated nature of the interaction between the Al_4^{2-} unit and other atoms/ions. Before the nature of the interaction of the Al_4^{2-} unit with other atoms/ions is understood, any attempt to calculate the RE of other Al_4^{2-}-containing molecules[8] is meaningless. The interaction between the Al_4^{2-} unit and other atoms/ions cannot be considered to be a simple single (or multiple) bond; we are currently studying the nature of this kind of interaction.

Al_4^{2-} has three independent delocalized bonding systems (one pure π bond and two σ bonds); each consists of four MOs and two electrons satisfying the $4n + 2$ electron counting rule of aromaticity and may be represented by four resonating bonding structures compared to C_6H_6, which has only one delocalized bonding system consisting of six π MOs and six electrons. Thus, Al_4^{2-} can be represented by $4 \times 4 \times 4 = 64$ potential resonating Kekulé-like structures; each Kekulé-like structure has three localized chemical bonds, compared to only two Kekulé structures representing C_6H_6. As a result, the resonance energy of Al_4^{2-} ($\sim$72.7 kcal/mol as the upper limit or $\sim$52.5 kcal/mol as the lower limit) is at least 2.5 times that of C_6H_6 (20 kcal/mol). We may reasonably conclude that the square planar structure of Al_4^{2-} has "3-fold" aromaticity. This is to emphasize that C_6H_6 has 1-fold aromaticity on the basis of the fact that only the delocalized π bonding system satisfies the $4n + 2$ electron counting rule. The 3-fold aromaticity of Al_4^{2-} is due to the presence of three independent delocalized bonding systems, one pure π bonding system and two σ bonding systems. Each of the three delocalized chemical bonding systems satisfies the $4n + 2$ electron counting rule of aromaticity. We also discussed the 2-fold aromaticity (one π plus one σ) of the Al_3^- anion, which can be represented by $3 \times 3 = 9$ potential resonating Kekulé-like structures, each with two localized chemical bonds.

Our finding leads to the suggestion, applicable to both organic and inorganic molecules, for examining delocalized chemical bonding that the possible electronic contribution to the aromaticity of a molecule should not be limited to only one particular delocalized bonding system satisfying a certain electron counting rule of aromaticity. More than one independent delocalized bonding system could simultaneously satisfy the electron counting rule of aromaticity, and therefore, a molecular structure could have multiple-fold aromaticity.

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