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On the Resonance Energy in New All-Metal Aromatic Molecules

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We have recently advanced the aromaticity concept into all-metal molecules containing Al_4^{2-}, XAl_3^-, Ga_4^{2-}, In_4^{2-}, Hg_4^{6-}, Al_3^-, and Ga_3^- aromatic units. All these systems are electron deficient species compared to the corresponding aromatic hydrocarbons. The electron deficiency results in an interesting new feature in all-metal aromatic systems, which should be considered as having both π- and σ-aromaticity, and that should result in their additional stability. In this work, we obtain crude evaluations of the resonance energies for Na_2Al_4 and Na_2Ga_4 all-metal aromatic molecules. The resonance energies were found to be unusually high: 30 kcal/mol (B3LYP/6-311+G*) and 48 kcal/mol (CCSD(T)/6-311+G(2df)) for Na_2Al_4 and 21 kcal/mol (B3LYP/6-311+G*) for Na_2Ga_4 compared to 20 kcal/mol in benzene. We believe that the high resonance energies in Na_2Al_4 and in Na_2Ga_4 are due to the presence of three completely delocalized bonds, one π-bond and two σ-bonds, thus confirming the presence of π- and σ-aromaticity.

Introduction

The aromaticity concept has been recently advanced into all-metal molecules containing Al_4^{2-}, XAl_3^-, Ga_4^{2-}, In_4^{2-}, Hg_4^{6-}, Al_3^-, and Ga_3^- aromatic units.[1-5] While Robinson and co-workers[6-8] in the middle of 90s synthesized organometallic compounds containing aromatic $-Ga_3^{2-}-$ groups bound to three bulky ligands and stabilized by two cations, our aromatic molecules containing only metal atoms are different. Robinson's compounds are valence isoelectronic with the aromatic hydrocarbon $C_3H_3^+$ cation. In fact, Schaefer and co-workers[7] used the $Ga_3H_3^{2-}$ model in ab initio calculations in order to prove the presence of a π-bond in Robinson's compounds. Our all-metal aromatic molecules have four valence electrons less than the corresponding aromatic hydrocarbon $C_4H_4^{2+}$ dication,[9] and therefore they are electron deficient aromatic systems. The electron deficiency results in an interesting new feature in our all-metal aromatic systems, which should be considered as having both π- and σ-aromaticity. In a recent article, Fowler and co-workers[10] evaluated ring current in Al_4^{2-} and MAl_4^- (M = Li, Na, Cu) and concluded that σ-electrons are responsible for the delocalized diamagnetic current induced by a perpendicular magnetic field. On the basis of analysis of aromatic ring-current shielding calculations, Sundholm and co-workers[11] concluded that π-electrons contribute to diatropic ring current, and thus our molecules are both σ- and π-aromatic. We arrived at the same conclusion from the analysis of the molecular orbitals.[1-5] We identified in Al_4^{2-} four MOs (HOMO-3, HOMO-4, HOMO-4′, HOMO-5, Figure 1a) corresponding to Al lone pairs (linear combinations of 3s-AO), two MOs (HOMO-1, HOMO-2) corresponding to σ-bonding, and one MO (HOMO) corresponding to π-bonding. All three bonding MOs are completely bonding-delocalized orbitals, and therefore they all should add extra stability to the all-metal aromatic systems. Such double or triple aromaticity (if two σ-bonds are considered separately) should result in much higher "resonance" or

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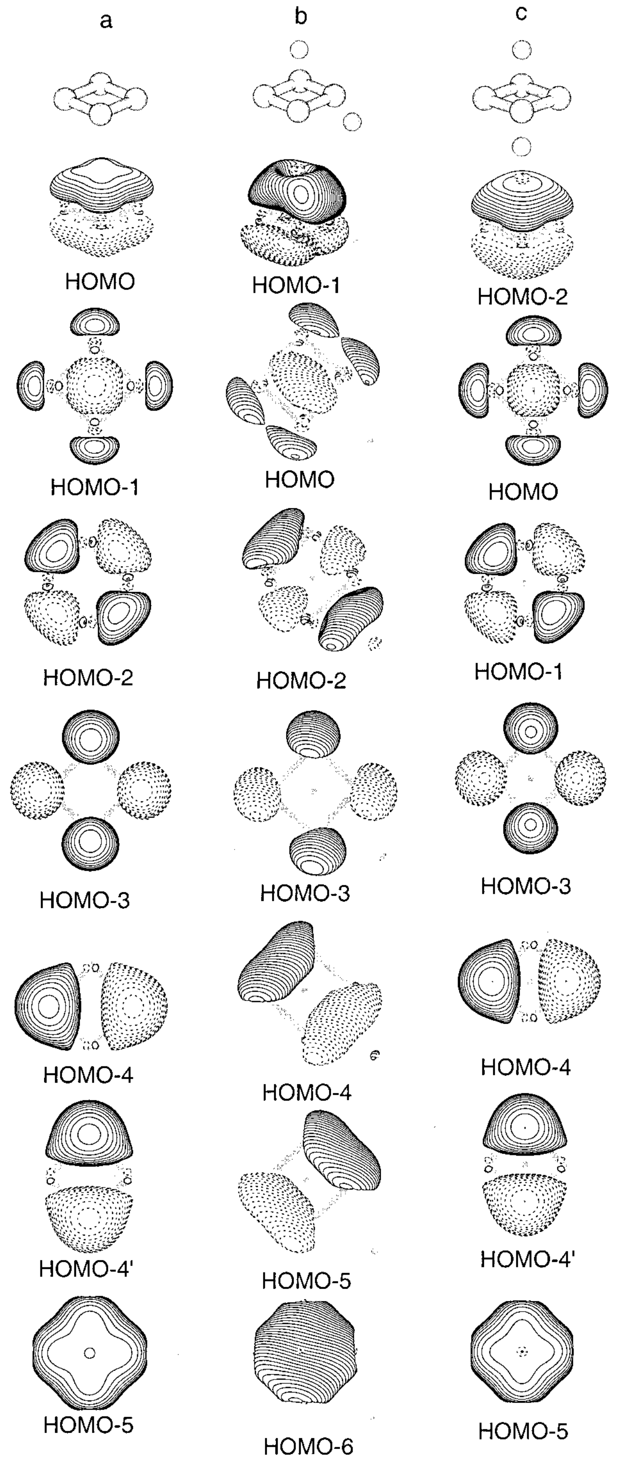

Figure 1. Molecular structure and molecular orbital pictures of (a) bare Al_4^{2-}, (b) Na_2Al_4 (C_s, $^1A'$), and (c) Na_2Al_4 (D_{4h}, $^1A_{1g}$).

stabilization energy in Na_2Al_4. However, it is very hard to evaluate accurately the resonance energy in the Na_2Al_4 molecule due to the interaction of Na^+ and Al_4^{2-} and due to the problem of identifying a suitable reference molecule with an Al═Al double bond formed by aluminum atoms with the valence I. Still, taking into account the importance of the resonance energy within the concept of aromaticity, we present in this article our crude evaluations of it in the context of the Na_2Al_4 and Na_2Ga_4 molecules.

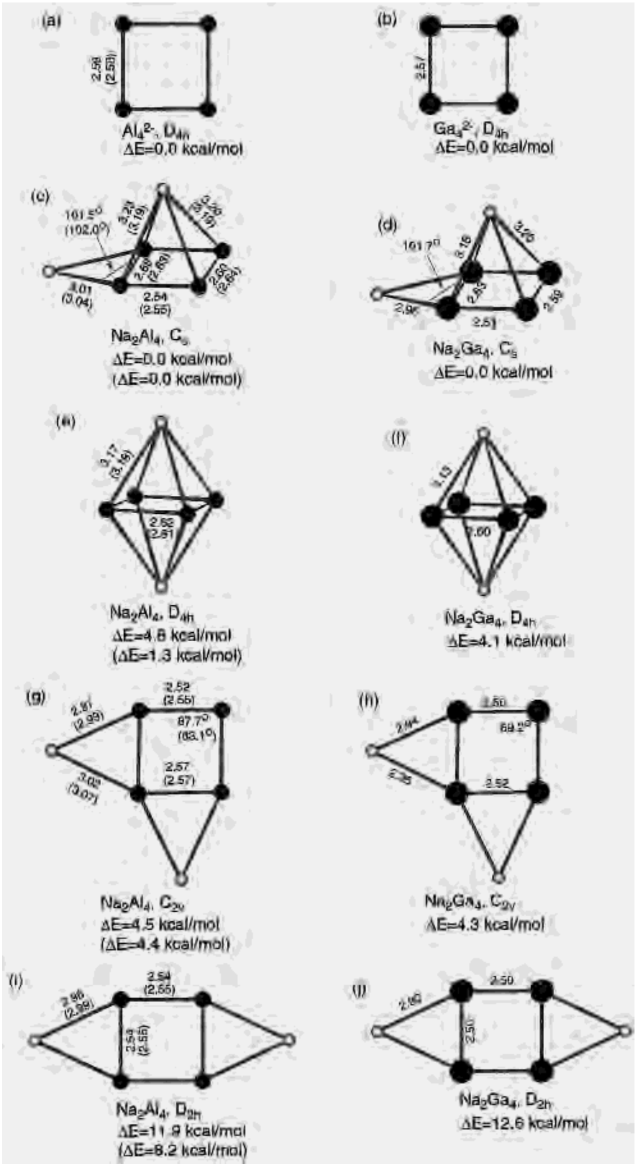

Figure 2. Optimized structures of (a) Al_4^{2-} (D_{4h}), (b) Ga_4^{2-} (D_{4h}), (c) Na_2Al_4 (C_s, $^1A'$), (d) Na_2Ga_4 (C_s, $^1A'$), (e) Na_2Al_4 (D_{4h}, $^1A_{1g}$), (f) Na_2Ga_4 (D_{4h}, $^1A_{1g}$), (g) Na_2Al_4 (C_{2v}, $^1A_1$), (h) Na_2Ga_4 (C_{2v}, $^1A_1$), (i) Na_2Al_4 (D_{2h}, ^1A_g), and (j) Na_2Ga_4 (D_{2h}, ^1A_g) at the B3LYP/6-311+G* and MP2/6-311+G* levels of theory. Data at MP2/6-311+G* are given in parentheses. Bond lengths are given in Å.

Computational Methods and Theoretical Results

We initially optimized geometries and calculated frequencies of Na_2Al_4 and Na_2Ga_4 species using analytical gradients with polarized split-valence basis sets (6-311+G*)[12-14] for Al and Ga and a hybrid method known in the literature as B3LYP.[15-17] The singlet structures with one Na^+ cation coordinated to the face and another one to the edge of the square-planar X_4^{2-} dianions (Figure 2c and 2d) were found

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Table 1. Calculated Molecular Properties of Na$_2$Al$_4$ Structures

Na$_2$Al$_4$ (C_s, ^{1}A′)[a]	B3LYP/ 6-311+G*	MP2/ 6-311+G*	Na$_2$Al$_4$ (D_{4h}, $^1\mathrm{A_{1g}}$)[b]	B3LYP/ 6-311+G*	MP2/ 6-311+G*
E_{tot}, au	−1294.416753	−1291.643940	E_{tot}, au	−1294.409509	−1291.641981
NIMAG	0	0	NIMAG	0	0
ν_1 (a′), cm^{-1}	348	353	ν_1 ($\mathrm{a_{1g}}$), cm^{-1}	283	307
ν_2 (a′), cm^{-1}	294	302	ν_2 ($\mathrm{a_{1g}}$), cm^{-1}	154	158
ν_3 (a′), cm^{-1}	250	295	ν_3 ($\mathrm{a_{2u}}$), cm^{-1}	182	187
ν_4 (a′), cm^{-1}	170	182	ν_4 ($\mathrm{b_{1g}}$), cm^{-1}	147	144
ν_5 (a′), cm^{-1}	166	177	ν_5 ($\mathrm{b_{2g}}$), cm^{-1}	289	295
ν_6 (a′), cm^{-1}	95	97	ν_6 ($\mathrm{b_{2u}}$), cm^{-1}	186	192
ν_7 (a′), cm^{-1}	43	42	ν_7 ($\mathrm{e_g}$), cm^{-1}	83	78
ν_8 (a″), cm^{-1}	311	391	ν_8 ($\mathrm{e_u}$), cm^{-1}	257	334
ν_9 (a″), cm^{-1}	161	174	ν_9 ($\mathrm{e_u}$), cm^{-1}	57	68
ν_{10} (a″), cm^{-1}	133	141			
ν_{11} (a″), cm^{-1}	79	90			
ν_{12} (a″), cm^{-1}	69	68			
ZPE, kcal/mol	3.029	3.305	ZPE, kcal/mol	2.909	3.207

[a] CCSD(T)/6-311+G(2df)//MP2/6-311+G*: $E_{\mathrm{CCSD(T)}} = -1291.739509$ au. [b] CCSD(T)/6-311+G(2df)//MP2/6-311+G*: $E_{\mathrm{CCSD(T)}} = -1291.739482$ au.

Table 2. Calculated Molecular Properties of Na$_2$Al$_4$ Structures

Na$_2$Al$_4$ (C_{2v}, $^1\mathrm{A_1}$)	B3LYP/ 6-311+G*	MP2/ 6-311+G*	Na$_2$Al$_4$ (D_{2h}, $^1\mathrm{A_g}$)	B3LYP/ 6-311+G*	MP2/ 6-311+G*
E_{tot}, au	−1294.409631	−1291.636830	E_{tot}, au	−1294.397765	−1291.630772
NIMAG	0	1	NIMAG	1	0
ν_1 ($\mathrm{a_1}$), cm^{-1}	332	380	ν_1 ($\mathrm{a_g}$), cm^{-1}	360	357
ν_2 ($\mathrm{a_1}$), cm^{-1}	315	327	ν_2 ($\mathrm{a_g}$), cm^{-1}	328	336
ν_3 ($\mathrm{a_1}$), cm^{-1}	182	190	ν_3 ($\mathrm{a_g}$), cm^{-1}	163	164
ν_4 ($\mathrm{a_1}$), cm^{-1}	133	148	ν_4 ($\mathrm{a_u}$), cm^{-1}	96	80
ν_5 ($\mathrm{a_1}$), cm^{-1}	35	49	ν_5 ($\mathrm{b_{1u}}$), cm^{-1}	292	361
ν_6 ($\mathrm{a_2}$), cm^{-1}	35	16	ν_6 ($\mathrm{b_{1u}}$), cm^{-1}	199	210
ν_7 ($\mathrm{b_1}$), cm^{-1}	94	107	ν_7 ($\mathrm{b_{2g}}$), cm^{-1}	38i	88
ν_8 ($\mathrm{b_1}$), cm^{-1}	48	13i	ν_8 ($\mathrm{b_{2u}}$), cm^{-1}	301	487
ν_9 ($\mathrm{b_2}$), cm^{-1}	364	360	ν_9 ($\mathrm{b_{2u}}$), cm^{-1}	67	89
ν_{10} ($\mathrm{b_2}$), cm^{-1}	296	353	ν_{10} ($\mathrm{b_{3g}}$), cm^{-1}	175	176
ν_{11} ($\mathrm{b_2}$), cm^{-1}	173	183	ν_{11} ($\mathrm{b_{3g}}$), cm^{-1}	58	56
ν_{12} ($\mathrm{b_2}$), cm^{-1}	121	134	ν_{12} ($\mathrm{b_{3u}}$), cm^{-1}	29	24
ZPE, kcal/mol	3.042	3.212	ZPE, kcal/mol	2.956	3.471

Table 3. Calculated Molecular Properties of Na$_2$Ga$_4$ Structures

Na$_2$Ga$_4$ (C_s, ^{1}A′)	B3LYP/6-311+G*	Na$_2$Ga$_4$ (D_{4h}, $^1\mathrm{A_{1g}}$)	B3LYP/6-311+G*
E_{tot}, au	−8024.165114	E_{tot}, au	−8024.158547
NIMAG	0	NIMAG	0
ν_1 (a′), cm^{-1}	224	ν_1 ($\mathrm{a_{1g}}$), cm^{-1}	184
ν_2 (a′), cm^{-1}	181	ν_2 ($\mathrm{a_{1g}}$), cm^{-1}	147
ν_3 (a′), cm^{-1}	170	ν_3 ($\mathrm{a_{2u}}$), cm^{-1}	166
ν_4 (a′), cm^{-1}	155	ν_4 ($\mathrm{b_{1g}}$), cm^{-1}	107
ν_5 (a′), cm^{-1}	139	ν_5 ($\mathrm{b_{2g}}$), cm^{-1}	175
ν_6 (a′), cm^{-1}	70	ν_6 ($\mathrm{b_{2u}}$), cm^{-1}	118
ν_7 (a′), cm^{-1}	40	ν_7 ($\mathrm{e_g}$), cm^{-1}	66
ν_8 (a″), cm^{-1}	192	ν_8 ($\mathrm{e_u}$), cm^{-1}	153
ν_9 (a″), cm^{-1}	113	ν_9 ($\mathrm{e_u}$), cm^{-1}	50
ν_{10} (a″), cm^{-1}	92		
ν_{11} (a″), cm^{-1}	63		
ν_{12} (a″), cm^{-1}	60		
ZPE, kcal/mol	2.141	ZPE, kcal/mol	2.051

Table 4. Calculated Molecular Properties of Na$_2$Ga$_4$ Structures

Na$_2$Ga$_4$ (C_{2v}, $^1\mathrm{A_1}$)	B3LYP/ 6-311+G*	Na$_2$Ga$_4$ (D_{2h}, $^1\mathrm{A_g}$)	B3LYP/ 6-311+G*
E_{tot}, au	−8024.158161	E_{tot}, au	−8024.145137
NIMAG	0	NIMAG	1
ν_1 ($\mathrm{a_1}$), cm^{-1}	215	ν_1 ($\mathrm{a_g}$), cm^{-1}	239
ν_2 ($\mathrm{a_1}$), cm^{-1}	198	ν_2 ($\mathrm{a_g}$), cm^{-1}	212
ν_3 ($\mathrm{a_1}$), cm^{-1}	162	ν_3 ($\mathrm{a_g}$), cm^{-1}	153
ν_4 ($\mathrm{a_1}$), cm^{-1}	106	ν_4 ($\mathrm{a_u}$), cm^{-1}	74
ν_5 ($\mathrm{a_1}$), cm^{-1}	43	ν_5 ($\mathrm{b_{1u}}$), cm^{-1}	200
ν_6 ($\mathrm{a_2}$), cm^{-1}	22	ν_6 ($\mathrm{b_{1u}}$), cm^{-1}	161
ν_7 ($\mathrm{b_1}$), cm^{-1}	71	ν_7 ($\mathrm{b_{2g}}$), cm^{-1}	47i
ν_8 ($\mathrm{b_1}$), cm^{-1}	29	ν_8 ($\mathrm{b_{2u}}$), cm^{-1}	187
ν_9 ($\mathrm{b_2}$), cm^{-1}	232	ν_9 ($\mathrm{b_{2u}}$), cm^{-1}	60
ν_{10} ($\mathrm{b_2}$), cm^{-1}	194	ν_{10} ($\mathrm{b_{3g}}$), cm^{-1}	129
ν_{11} ($\mathrm{b_2}$), cm^{-1}	153	ν_{11} ($\mathrm{b_{3g}}$), cm^{-1}	53
ν_{12} ($\mathrm{b_2}$), cm^{-1}	91	ν_{12} ($\mathrm{b_{3u}}$), cm^{-1}	24
ZPE, kcal/mol	2.166	ZPE, kcal/mol	2.132

to be global minima. The Na$_2$Al$_4$ structures were refined using the MP2/6-311+G* level of theory.[18] The optimized geometries and vibrational frequencies agreed well at the B3LYP/6-311+G* and MP2/6-311+G* levels of theory for all Na$_2$Al$_4$ structures (Figure 2 and Tables 1−4). Finally, the two most stable structures of Na$_2$Al$_4$ were further studied using the coupled-cluster method [CCSD(T)][19−21] with the extended 6-311+G(2df) basis sets. The (C_s, ^{1}A′) structure with one cation coordinated to the face Al$_4^{2-}$ and another one coordinated to the edge was found to be the most stable. To test further the validity of the one-electron approximation, we performed a single-point CASSCF(6,8)/6-311+G* calculation of Na$_2$Al$_4$ with six active electrons and eight active molecular orbitals using the B3LYP/6-311+G* geometry. We found that the Hartree−Fock configuration is domi-

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Table 5. Calculated Energies of Selected Reactions

reaction	B3LYP/6-311+G*	CCSD(T)/6-311+G(2df)
Na_2Al_4 (C_s, $^1A'$) → 2Na (^2S) + 4Al (^2P)	+184 kcal/mol[a]	+214 kcal/mol[a]
$H_2Al-AlH_2$ → $2AlH_2$	+56 kcal/mol	+60 kcal/mol
Na_2Al_4 (C_s, $^1A'$) → NaAl ($C_{\infty v}$, $^1\Sigma^+$) + $NaAl_3$ (C_{3v}, $^1A_1$)	+78 kcal/mol	+97 kcal/mol

[a] Corrected for zero-point energy at the B3LYP/6-311+G* level of theory.

nant: $C_{HF} = 0.9045$. Thus, the one-electron bonding picture is expected to be valid.

All calculations were performed using the Gaussian 98 program.[22] Pictures of the Hartree−Fock MOs (RHF/6-311+G*) are made with the help of the MOLDEN program.[23]

Bonding in Na_2Al_4 and Na_2Ga_4. The MOs of Al_4^{2-} of the two most stable structures of Na_2Al_4 are presented in Figure 1. One can see that the role of Na^+ is to stabilize an otherwise electronically unstable Al_4^{2-} dianion; it has relatively minor effects on the electronic structure of the dianion. The HOMO ($1a_{2u}$) of Al_4^{2-} is formed from the out-of-plane $3p_z$ orbitals (Figure 1a). The HOMO-1 ($2a_{1g}$) and HOMO-2 ($1b_{2g}$) are bonding orbitals formed from the in-plane $3p_{x,y}$ orbitals. The following four MOs are bonding, nonbonding, and antibonding orbitals formed primarily from the filled 3s valence orbitals of Al. When all bonding, nonbonding, and antibonding MOs composed of the same atomic orbitals (such as the 3s orbitals of Al in this case) are occupied, the net bonding effect is expected to be close to zero, and the atomic orbitals can be viewed approximately as lone pairs. This fact can be understood better using He_2 as an example. In the He_2 dimer, both bonding $(1s_{He1} + 1s_{He2})^2$ and antibonding $(1s_{He1} - 1s_{He2})^2$ MOs are occupied; therefore, the net bonding effect is zero and the $1s^2$ orbital at each He atom can be treated as a lone (nonbonding) pair.

In the Na_2Al_4 species, the MOs of the Al_4^{2-} dianion can be easily recognized, and the same is true for Ga species. However, if we compare the nature of our aromatic all-metal M_4^{2-} (M = Al, Ga) species with a reference organic aromatic $H_4C_4^{2+}$ cation,[9] we find that although all these species possess two π-electrons and are aromatic, they are not isoelectronic. The square-planar all-metal systems have 14 valence electrons, while the aromatic $H_4C_4^{2+}$ has 18 valence electrons. The four valence electron deficit in our all-metal M_4^{2-} systems has important consequences. In $H_4C_4^{2+}$, there are eight classical two-center, two-electron bonds (the four C−H bonds and the four C−C bonds) plus one delocalized four-center π-bond that gives rise to aromaticity in this species.[9] On the other hand, the all-metal M_4^{2-} clusters have only seven pairs of electrons each. Four pairs can be assigned to four lone pairs of M, as discussed earlier. One pair is the delocalized four-center π-bond, and only two pairs of electrons are available for σ-bonds. Therefore, one cannot draw the classical structure for M_4^{2-} with four two-center two-electron bonds. These systems are electron deficient. Only Al−Al σ-bonding MOs having multicenter bonding properties are occupied. The only possible representation using the classical two-center two-electron language for these systems is through the 12 resonance structures discussed in our previous work.[3] The average M−M bond order in these metallic clusters is only 0.75, resulting from the three bonding MOs (two σ- and one π-bond) divided among the four M−M bonds in the M_4^{2-} square.

Evaluation of the Resonance Energies in Na_2Al_4 and Na_2Ga_4. On the basis of the bonding picture, we now can try to evaluate the resonance energy in the Na_2Al_4 and Na_2Ga_4 molecules. We need to introduce a few approximations in order to achieve our goal. First, we will assume that Al and Ga atoms have valence I and there is little hybridization mixing between s- and p-AOs in these atoms. Second, we cannot devise a molecule where Al will have valence I and yet has a double bond. Therefore, we assume that an Al═Al double bond is equal in strength to two Al−Al single bonds. (Ab initio evaluation of the Al═Al bond shows[24] that it is expected to be weak, and therefore the second assumption may only decrease the evaluated resonance energy). Third, we assume that the energy of the Na−Al_4 bond in Na_2Al_4 is approximately equal to the energy of the Na−Al bond in the NaAl diatomic molecule. We understand that these assumptions are rather approximate and therefore our resonance energy evaluations will be rather crude.

We calculated the atomization energies for the Na_2Al_4 most stable structures at two levels of theory (see Table 5).

$$Na_2Al_4(C_s, {}^1A') \rightarrow 2Na({}^2S) + 4Al({}^2P) \qquad (1)$$

The energy of the Na−Al bond is 17 kcal/mol (B3LYP/6-311+G*) and 18 kcal/mol (CCSD(T)/6-311+G(2df)).

The needed energy of the Al−Al single bond is not readily available. The dissociation energy of $H_2Al-AlH_2$ is not appropriate because it involves dissociation of the Al−Al bond with two Al atoms in valence III rather than valence I. However, the $Al-AlH_2$ molecule contains an Al−Al bond, with one Al being in the valence I state and the other in valence III. From eq 2, we can evaluate an Al−Al bond energy in a hypothetical Al_2 molecule, which has an Al−Al single bond, formed from only $3p_\sigma$-AOs.

$$Al-Al + H_2Al-AlH_2 \rightarrow 2Al-AlH_2 \qquad (2)$$

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We remind the reader that Al_2 has a triplet ground electronic state ($^3\Pi_u$)[25] with one electron occupying a σ-MO and another in a π-MO. Assuming that the energy of reaction 2 is zero and using our ab initio data for Al−AlH_2 and H_2-Al−AlH_2, we can calculate the energy of the desirable Al−Al single bond: 24 kcal/mol (B3LYP/6-311+G*) and 27 kcal/mol (CCSD(T)/6-311+G(2df)). (All these numbers have been corrected for ZPE.) Now we can evaluate the resonance energy from eq 3:

$$E_{at}(Na_2Al_4) - 2E_{diss}(Na-Al) - 3E_{diss}(Al-Al)E_{res} = +78 \text{ kcal/mol (B3LYP/6-311+G*)} \quad (3)$$

$$E_{res} = +97 \text{ kcal/mol (CCSD(T)/6-311+G(2df))}$$

While our resonance energy depends on the theoretical method, these results are certainly unexpectedly high on the basis of the value of the resonance energy in benzene E_{res} = 20 kcal/mol.[26] We believe that these numbers, which we will call "optimistic", are unrealistically high. They can be substantially reduced if we take into account the s−p hybridization of Al atoms in Na_2Al_4. The influence of the s−p hybridization on the Al−Al bond energy can be obtained from the $H_2Al-AlH_2$ molecule, where the dissociation occurs into two AlH_2 groups (see Table 5). With these Al−Al bond energies, the resonance energy in Na_2Al_4 will be −18 kcal/mol (B3LYP/6-311+G*) and −2 kcal/mol (CCSD(T)/6-311+G(2df)). Certainly, these numbers, which we will call "pessimistic" are unrealistically low because Al atoms in Na_2Al_4 are not sp^2 hybridized as in Al_2H_4.

One way to evaluate an approximate degree of hybridization is to consider the effective occupation numbers of atomic orbitals. We calculated the effective occupation numbers of atomic orbitals according to the natural population analysis. These numbers were found to be $3s^{1.54}3p_\sigma^{1.34}3p_\pi^{0.45}$ for Al in Na_2Al_4 compared to $3s^{1.88}3p_\sigma^{0.73}$ for Al^I and $3s^{1.17}3p_\sigma^{1.32}$ for Al^{III} in Al−AlH_2. We estimate that the degree of hybridization of Al in Na_2Al_4 is between these two extremes. We believe that a more realistic resonance energy can be obtained by averaging the optimistic and pessimistic values. In doing so we now have a "realistic" resonance energy for Na_2Al_4: 30 kcal/mol (B3LYP/6-311+G*) and 48 kcal/mol (CCSD(T)/6-311+G(2df)). A similar analysis reveals that the realistic resonance energy for Na_2Ga_4 is 21 kcal/mol (B3LYP/6-311+G*).

We can further test our numbers by using the Al−Al bond energy from the Al_2 diatomic molecule, D_0 = 30 kcal/mol (B3LYP/6-311+G*) and D_0 = 32 kcal/mol (CCSD(T)/6-311+G(2df)), which is close to the experimental value: D_0 = 31 kcal/mol.[27] The valence electronic configuration for Al_2 ($1\sigma_g^2 1\sigma_u^2 2\sigma_g^1 1\pi_u^1$) shows that the first two MOs are bonding and antibonding orbitals composed from 3s-AOs, while the last two are σ-bonding ($2\sigma_g$) and π-bonding ($1\pi_u$) orbitals composed from $2p_z$-AO and $2p_{x \text{ or } y}$-AOs of Al. Therefore, if both bonding orbitals are occupied by a single electron, the bond order in Al_2 ($^3\Pi_u$) can be taken to be approximately 1. On the basis of these values for the Al−Al bond, we can compare the resonance energy (assuming that we have to break three Al−Al bonds and two Na−Al bonds in Na_2Al_4): 60 kcal/mol (B3LYP/6-311+G*) and 82 kcal/mol (CCSD(T)/6-311+G(2df). These numbers are close to the optimistic values of the resonance energy quoted above.

We can also test the validity of the assumption that the Na−Al bond energy represents the Na−Al_4Na bond energy. To evaluate the Na−Al_4Na bond energy, we optimized the geometry of the $NaAl_4$ pyramidal structure. We found that it has one imaginary frequency for the (C_{4v}, $^2B_1$) structure. Geometry distortion along the imaginary frequency normal mode leads to the (C_{2v}, $^2A_1$) structure, which is a pyramidal geometry with Na^+ coordinated to the face of the rhombus structure of Al_4^-. The dissociation energy of Na_2Al_4(C_s, $^1A_1$) → Na(^2S) + $NaAl_4$(C_{2v}, $^2A_1$) was found to be 33 kcal/mol (B3LYP/6-311+G*) and 39 kcal/mol (CCSD(T)/6-311+G-(2df). These numbers are overestimated because when the Na−Al_4Na bond is breaking, the departing sodium atom takes its electron from the bonding four-center Al−Al bond. If we use these values for the sodium−aluminum bond and Al−Al bond energies from the Al_2 ($^3\Pi_u$) molecule, the resonance energy is 25 kcal/mol (B3LYP/6-311+G*) and 41 kcal/mol (CCSD(T)/6-311+G(2df)). These numbers are close to the realistic values quoted above.

However, even these realistic numbers are rather high considering that the resonance energy in Na_2Al_4 is 100% (B3LYP/6-311+G*) and 150% (CCSD(T)/6-311+G(2df)) relative to the dissociation energy of Al_2. We remind the reader that the resonance energy in benzene is just 25% of the C−C bond energy.[26] We believe that the high resonance energy in Na_2Al_4 is due to the presence of three completely delocalized bonds: one π-bond and two σ-bonds. If we divide the resonance energy by a factor of 3, the resonance energy per bond will be just 8 kcal/mol (B3LYP/6-311+G*) and 16 kcal/mol (CCSD(T)/6-311+G(2df)), which seems rather reasonable.

Some additional sense of the extra stability of in Na_2Al_4 due to its aromaticity can also be evaluated from the energy of reaction 4 (see Table 5):

$$Na_2Al_4(C_s, {}^1A') \rightarrow NaAl(C_{\infty v}, {}^1\Sigma^+) + NaAl_3(C_{3v}, {}^1A_1) \quad (4)$$

We have previously shown[5] that a $NaAl_3$ molecule contains an aromatic Al_3^- anion which has one delocalized σ- and one delocalized π-bond. Therefore, from Na_2Al_4 to $NaAl_3$, we lose one delocalized σ-bond, and the degree of delocalization in the two remaining bonds is diminished from four to three atoms. One can see that the energy of reaction 4 is rather high, thus confirming very strong bonding in Na_2Al_4 and, indirectly, its high resonance energy.

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Conclusions

We have obtained crude evaluations of the resonance energy for Na_2Al_4 and Na_2Ga_4 all-metal aromatic systems. The resonance energies were found to be unusually high: 30 kcal/mol (B3LYP/6-311+G*) and 48 kcal/mol (CCSD(T)/6-311+G(2df)) for Na_2Al_4 and 21 kcal/mol (B3LYP/6-311+G*) for Na_2Ga_4 compared to 20 kcal/mol in benzene. We believe that the high resonance energy in Na_2Al_4 is due to the presence of three completely delocalized bonds, one π-bond and two σ-bonds, and thus our all-metal aromatic systems are both π- and σ-aromatic.

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