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TWO SIDES OF A STORY

A Deeper Discussion Of All-Metal Aromaticity-Antiaromaticity

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A lively discussion has ensued on whether newly reported all-metal compounds, such as Li_3Al_4^- , can be considered truly antiaromatic or are actually net aromatic.

On the one hand, associate chemistry professor Alexander I. Boldyrev of Utah State University, physics professor Lai-Sheng Wang of Washington State University's Tricities campus and Pacific Northwest National Laboratory, and their colleagues find that the Al_4^{4-} ring in Li_3Al_4^- contains four π electrons and has a nonequilateral (rectangular) shape. They believe the deviation from an equilateral (square) ring, which would be expected for an aromatic compound, confirms that the compound is antiaromatic [[C&EN, April 28, page 8](#); *Science*, **300**, 622 (2003)].

On the other hand, chemistry professor [Paul v. R. Schleyer](#) and postdoctoral researcher [Zhongfang Chen](#) of the University of Georgia and the University of Erlangen-Nuremberg, in Germany, and coworkers assert that the Li_3Al_4^- bonding picture painted by Boldyrev and Wang is an incomplete view [[J. Am. Chem. Soc.](#), **125**, 13930 (2003)]. [Schleyer](#) and [Chen](#) agree with Boldyrev and Wang that the Al_4^{4-} unit is π antiaromatic. But they contend that the minor differences in Al-Al bond lengths are unimportant and that the antiaromaticity is overwhelmed by the ring's σ aromaticity, meaning that overall, the compound is aromatic.

The finer details of the debate unfolded in a series of recent back-and-forth e-mail exchanges between [Schleyer and Chen \(S&C\)](#) and Boldyrev and Wang (B&W), which were channeled through C&EN. Part of what unfolded is as follows:

S&C: If Li_3Al_4^- were antiaromatic and destabilized, as claimed, it would adopt a different structure. Nonplanarity and other distortions ameliorating repulsive interactions are characteristics of antiaromatic

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A Deeper Discussion Of All-Metal Aromaticity-Antiaromaticity

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systems. In contrast, the Al–Al bond lengths in the Al_4^{4-} cluster differ by only 10% or less, in contrast to the nearly 20% difference in the much stronger C–C bonds in cyclobutadiene. Thus, an additional critical analysis of the geometry favors our interpretation that the aromatic σ effect dominates.

B&W: We would agree that aromaticity overwhelms antiaromaticity in Li_3Al_4^- if the geometric structure of the Al_4^{4-} unit were a square, as it is in the aromatic Al_4^{2-} dianion. Certainly, the C–C σ bond is stronger than the Al–Al σ bond. Although percentwise the distortion from the square structure is smaller, the absolute alteration in the Al–Al bonds in Li_3Al_4^- is 0.24 Å on average, which is comparable to the 0.23-Å alteration in cyclobutadiene at the same level of theory. The point here is that there is bond alteration at all. S&C agree that the Al_4^{4-} unit in Li_3Al_4^- has a rectangular structure, with slight distortions from an ideal rectangle due to asymmetric capping by Li^+ . Therefore, the σ aromaticity does not overwhelm the π antiaromaticity from the geometric point of view.

S&C: Aromaticity depends very little on the bond lengths. B&W are confusing the proclivity of strong C–C single bonds toward favoring "standard" distances with the expected behavior of the weaker, electron-deficient Al–Al σ bonds. This is substantiated by the calculated frequencies of the ring breathing-mode vibrations (C–C versus Al–Al): 952 cm^{-1} for neutral cyclobutadiene versus only 237 cm^{-1} for neutral Li_4Al_4 .

B&W: If Li_3Al_4^- were aromatic, the vertical electron detachment energy (VDE) determined by photoelectron spectroscopy should be about the same as in the aromatic LiAl_4^- anion. However, our data show that the first VDE of Li_3Al_4^- (1.39 eV) is substantially lower than the first VDE of LiAl_4^- (2.19 eV). This is a direct experimental confirmation of the antiaromatic nature of Li_3Al_4^- .

S&C: Not so at all. Because of the higher Coulomb repulsion of the Al_4^{4-} core than the Al_4^{2-} core, the VDEs of tetraanion-based species obviously should be lower than those of dianion-based Al_4^{2-} species. B&W are comparing the sizes of apples with watermelons.

B&W: We compared a singly charged anion LiAl_4^- with the singly charged anion Li_3Al_4^- . We think we are comparing apples with apples. On a different note, nucleus-independent chemical shift (NICS) indexes were initially proposed as one criterion for detecting π aromaticity. They work rather well for that purpose, and they are certainly applicable to our all-metal aromatic Al_4^{2-} and antiaromatic Al_4^{4-} as far as the π orbitals are concerned. However, we have doubts that the NICS indexes can be used as a probe for σ aromaticity.

S&C: Why? B&W should examine our use of NICS to characterize σ antiaromaticity as well as σ aromaticity: " σ -Antiaromaticity in Cyclobutane, Cubane, and Other Molecules with Saturated Four-Membered Rings" [*Org. Lett.*, **5**, 23 (2003)]. NICS gives the correct induced magnetic fields. Note that the induced field has contributions from all electrons--that is, from all molecular orbitals. Contributions

come from core, σ , and σ electrons.

B&W: In particular, we would like to point out that the NICS indexes presented in S&C's *JACS* paper are inconsistent with the nature of the molecular orbitals, which describe chemical bonding in Al_4^{4-} and Al_4^{2-} . According to NICS, the aromatic contributions in Li_3Al_4^- come primarily from the four low-lying molecular orbitals, which are linear combinations of the 3s lone pairs of the four aluminum atoms. That does not make sense to us.

S&C: These are by no means "lone pairs." This is a perfectly Hückel-like bound orbital. If these were lone pairs, B&W should explain the low energy, which is far below the 3s energy of Al.

B&W: From S&C's paper, we can see that the NICS for these four orbitals contribute -22.7 ppm to the overall σ aromaticity. Therefore, it's the aromaticity from the lone pairs that overwhelms the paramagnetic contributions from the antiaromatic π orbitals! The lone pairs do not contribute significantly to the net chemical bonding, and yet they are major contributors to the aromaticity?

S&C: B&W confuse local diatropic and paratropic shielding contributions with "aromaticity" and "antiaromaticity," respectively. The latter are associated with cyclic diamagnetic and paramagnetic circulation of electrons in rings, not in lone pairs or localized bonds. NICS analyses in terms of localized MOs (lone pairs and bonds) as well as canonical MO contributions differentiate and identify the pertinent MOs. This is described in detail in our papers, most recently in "Analysis of Aromatic Delocalization: Individual Molecular Orbital Contributions to Nucleus-Independent Chemical Shifts," [*J. Phys. Chem. A*, **107**, 6470 (2003)].

B&W: We also would like to point out that the two σ -aromatic orbitals in Al_4^{2-} and $\text{Li}_3\text{Al}_4^{4-}$, which are responsible for chemical bonding and σ aromaticity, make a total paramagnetic contribution (6.9 ppm in Al_4^{2-} and 4.9 ppm in Li_3Al_4^-). Hence, according to the NICS indexes, the σ bonding and aromatic orbitals contribute to antiaromaticity rather than to aromaticity! On the basis of this apparent contradiction, we suspect that the NICS indexes cannot properly describe σ aromaticity in the current form and should not be used for probing σ aromaticity.

S&C: Not so, as is shown in the *Journal of Physical Chemistry A* paper. The upper MOs, both π and especially σ , have more nodes and consequently make paratropic contributions. These do not, however, overcome the total diatropic contribution sum of the lower energy σ MOs. The strength of the binding energy of the molecule is the difference of the orbital energies of the atoms and the orbital energies of the molecule. Therefore, the low-energy valence orbitals usually have the largest contribution to the binding energy, while the high-energy orbitals have either no or little contribution or are even antibonding. NICS shows that low-energy σ and π orbitals are both diatropic, in agreement with the energetic point of view. Also, the energies of the first π MOs of aromatic molecules are lower than the p orbital energy of the free atom.

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