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DECIPHERING METAL ANTIAROMATICITY

Assessments of σ and π bonding in all-metal clusters draw chemists into an engaging debate

[STEPHEN K. RITTER, C&EN WASHINGTON](#)

Aromatic compounds--stabilized by $4n + 2 \pi$ electrons--were once thought to be purely the domain of organic chemistry. But this organic boundary has become flexible in the past few years as several research groups have shown that inorganic cluster systems can be aromatic.

The push to better understand the bonding in these compounds led earlier this year to the discovery that they can also possess antiaromaticity: destabilization observed in cyclic systems with $4n \pi$ electrons. Now, a lively discussion has ensued on whether the newly reported antiaromatic compounds are truly antiaromatic or are actually net aromatic.

The debate is centered on the work of 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. Boldyrev and Wang, as an extension of their earlier work on gas-phase, all-metal aromatic compounds, prepared and isolated the antiaromatic Li_3Al_4^- by laser vaporization of a LiAl alloy followed by time-of-flight mass spectrometry [[C&EN, April 28, page 8](#); *Science*, **300**, 622 (2003)].



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ANTIAROMATIC Wang (left) and Boldyrev believe that the observed four π electrons and computed unequal Al–Al bond lengths provide evidence of the overall antiaromaticity of Li_3Al_4^- and related species.
PNNL PHOTO

AROMATIC Schleyer (left) and Chen's computed magnetic susceptibilities indicate that the σ aromaticity in Li_3Al_4^- and related species overwhelms the π antiaromaticity, making the all-metal compounds net aromatic.
PHOTO BY KANG-NIAN FAN

Based on photoelectron spectroscopy and computational studies, which provided molecular orbitals and geometrical structures, they concluded 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.

The challenge to this antiaromaticity claim comes from 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 [*J. Am. Chem. Soc.*, 13930 (2003)]. They assert that the Li_3Al_4^- bonding picture painted by Boldyrev and Wang is an incomplete view.

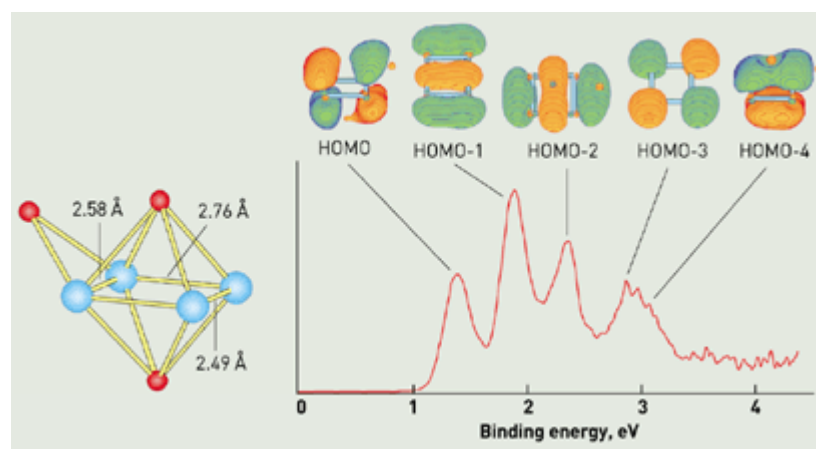
In a nutshell, Schleyer and Chen agree with Boldyrev and Wang that the Al_4^{4-} unit is π antiaromatic. But they contend that the minor differences in Al–Al bond lengths are unimportant and that the antiaromaticity is overwhelmed by the ring's σ aromaticity, meaning that overall, the compound is aromatic. In the *JACS* paper, Schleyer and Chen provide evidence for their claim in a series of computations of the induced magnetic shielding of Li_3Al_4^- and related species.

Attempting to sort out this conundrum has led to a growing discussion in the community of theoretical chemists who dabble in predicting the properties of unexpected compounds. Some observers suggest that because most of these compounds are currently available only in the gas phase, they are of minor significance and peripheral to the aromaticity-antiaromaticity debate. Still, others are exploring the intricate chemical bonding in the hope that these curious compounds eventually could be useful building blocks in semiconducting or superconducting materials. Irrespective of which "maticity" view turns out to be correct, this discourse is challenging chemists to move their work to a higher level.

Asked to comment on the debate, chemistry professor [Gernot Frenking](#) of Philipps University, Marburg, Germany, who studies the structure and bonding of transition-metal compounds, provided a succinct synopsis: "The papers by Boldyrev and Wang and Schleyer and Chen are exciting, and they will certainly trigger a new round of discussions about aromaticity.

"Using the magnetic properties of Li_3Al_4^- , Schleyer and Chen show convincingly that σ aromaticity plays an important role in the electronic structure," Frenking adds. "According to their data, the paramagnetic (antiaromatic) contributions of the π electrons are overcome by the diamagnetic (aromatic) contributions of the σ electrons. However, the calculated Al–Al bond lengths by Boldyrev and Wang suggest that the π -

antiaromatic character of Li_3Al_4^- may be stronger than the σ aromaticity, if the energy contributions rather than the magnetic contributions are considered."



PARAMAGNETIC VIEW Boldyrev and Wang compute the structures and molecular orbitals of all-metal systems and correlate the data to the compounds' photoelectron spectra. For Li_3Al_4^- , its four π electrons and rectangular Al_4^{4-} framework indicate that it is π antiaromatic. One set of π electrons resides in the delocalized HOMO-4, which has a minor contribution to the overall aromaticity. The second set resides in the HOMO, where the visible nodes in the electron density indicate antibonding breaks. The compound also has delocalized σ electrons (HOMO-1 and HOMO-2) that give rise to σ aromaticity. Overall, the four π electrons, the nature of the HOMO, and the unequal Al–Al bond lengths indicate that Li_3Al_4^- is antiaromatic. HOMO-3 and other higher energy orbitals (not shown) house Al lone pairs.

A LITTLE HISTORY is needed to set the stage for the particulars of the debate. In 2001, Boldyrev and Wang prepared a number of gas-phase aromatic bimetallic clusters with four-membered rings, such as the square pyramidal LiAl_4^- . The molecule consists of a planar Al_4^{2-} ring capped with a Li^+ cation, and it contains two π electrons ([C&EN, Sept. 24, 2001, page 39](#)). Altogether, Boldyrev and Wang have made a significant set of aromatic bimetallic clusters, including NaGa_4^- , NaIn_4^- , Na_6Hg_4 , MAl_4^- (M = Li, Na, and Cu), and MAl_3^- (M = Si, Ge, Sn, and Pb). The team also has prepared CAl_3^- , but the two π electrons in this case are localized on the more electronegative carbon, so the compound is nonaromatic.

Boldyrev and Wang subsequently were challenged by their colleagues and other researchers in the field to prepare analogous antiaromatic compounds. They reasoned that if the Al_4^{2-} anion could take on two additional π electrons, it would be antiaromatic. That led to the preparation of Li_3Al_4^- .

Schleyer, Chen, and coworkers make their claim for the aromaticity of Li_3Al_4^- on the basis of nucleus-independent chemical shift (NICS) indexes, a "simple and efficient aromaticity probe" devised by Schleyer

several years ago that is based on the magnetic properties of compounds. Although simple π -electron counting and equilateral bonding are general measures of aromaticity, Schleyer says, it is difficult to apply these criteria to inorganic clusters. However, the magnetic properties generated by cyclic delocalization of σ or π electrons in ring systems when exposed to an applied magnetic field--ring currents--are more reliable.

A chemical system is aromatic if it sustains an induced ring current that leads to a diamagnetic shift--a decrease in the magnetic susceptibility of the compound. For antiaromatic compounds, the shift in ring current is in the opposite direction, referred to as a paramagnetic shift.

The magnetic properties arising from ring currents can be experimentally measured as magnetic susceptibilities of compounds or as displaced chemical shifts in the ^1H nuclear magnetic resonance spectra of organic compounds. Schleyer developed NICS as a computational method to provide an indirect theoretical probe of ring currents to serve as a more definitive measure of aromaticity and antiaromaticity.

The calculated NICS indexes are based on the "absolute magnetic shielding" taken at the center of a ring compound, where the full effect of the induced ring current should be observed. The calculated NICS indexes with negative values are aromatic, and those with positive values are antiaromatic. The method is now widely used and has proven to be very accurate for traditional organic compounds as well as inorganic compounds such as the benzene analogs Ge_6H_6 and P_6 . A further attribute of the NICS method is that the total NICS value for a compound can be divided into contributions from the π orbitals and the σ orbitals.

This is not the first time the lives of these researchers have touched one another. Boldyrev, originally from Russia, was a Humboldt Fellow in the early 1990s in Schleyer's group in Germany. Schleyer and Boldyrev pursued calculations that explored a number of hypothetical planar clusters. However, no one expected that these compounds could be synthesized.

Boldyrev's career then took him to Utah State, where he continued theoretical work on the compounds, even though he could not find a collaborator who could synthesize any of them. In the late 1990s, he eventually teamed with Wang, and they were able to prepare some planar tetracoordinate carbon compounds, such as CAI_3Si^- , where the carbon atom sits at the center of the Al_3Si ring ([C&EN, Aug. 21, 2000, page 8](#)). The experiments finally substantiated the computational work and led Boldyrev and Wang down a path to discover their aromatic and antiaromatic compounds.

In Boldyrev and Wang's studies on the aromatic Al_4^{2-} compounds, they concluded that the overall aromaticity is related in part to two π electrons in a delocalized orbital and in part to the nature of the σ bonding. One of the molecular orbitals (MOs) for Al_4^{2-} (14 valence electrons) has the two π electrons in a completely delocalized bond spread over all four Al atoms. The other valence molecular orbitals include two σ bonds and ones containing a lone pair for each Al atom.

To explain the σ bonds in this electron-deficient ring system, Boldyrev and Wang proposed that there must be two delocalized σ -bonding orbitals spread across all four Al atoms--called σ aromaticity--rather than four classical two-electron, two-atom σ -bonding orbitals. All of the parties to the current debate agree on this description of the bonding in Al_4^{2-} compounds.

"IT'S REMARKABLE that Al_4^{2-} and its heavier congeners are doubly aromatic, with both π and σ aromaticity, which is different from hydrocarbon aromatic molecules," Boldyrev told C&EN in 2001.

For Li_3Al_4^- (with 16 valence electrons), the most stable structure is a "capped octahedron," which consists of the rectangular Al_4^{4-} ring with one lithium atom above and one lithium atom below the plane. The third lithium atom is outside the octahedron opposite one of the geometric faces. Boldyrev and Wang propose that the lowest valence MOs in Al_4^{4-} are similar to those in Al_4^{2-} , with one completely delocalized π orbital, an orbital for each Al lone pair, and the two delocalized σ orbitals.

The extra pair of π electrons for Li_3Al_4^- enter the highest occupied molecular orbital of Al_4^{4-} , which has nodes that separate two Al atoms on one side of the ring from the two Al atoms on the other side of the ring. In this orbital, bonding occurs between the Al atoms on the short sides of the ring, while the region between the Al atoms on the long sides is antibonding. Boldyrev and Wang point out that the rectangular ring and orbitals of Al_4^{4-} are similar to cyclobutadiene (C_4H_4)--the quintessential antiaromatic molecule.

For Schleyer and Chen's part, their NICS values for Al_4^{2-} are large and negative (diamagnetic), indicative of σ and π aromaticity, in agreement with Boldyrev and Wang. The total NICS value is -30.9 ppm, the sum of the NICS values for the σ MOs is -11.1 ppm, and the delocalized π MO is -17.8 ppm.

The picture for Li_3Al_4^- also matches that found by Boldyrev and Wang: The sum of the NICS values of the σ MOs is diamagnetic at -16.8 ppm, indicating aromaticity, and the sum of the π MOs is positive at 14.2 ppm, indicating antiaromaticity. However, Schleyer and Chen say their data show that the σ effect overpowers the π effect, as evidenced by the negative total NICS value of -4.8 ppm. Thus, they believe that overall Li_3Al_4^- should be considered aromatic. For comparison, the total NICS values for benzene and cyclobutadiene are -9.7 and 27.6 ppm, respectively.

The debate between Schleyer and Chen and Boldyrev and Wang was carried out in greater detail through a series of recent back-and-forth e-mail exchanges that were channeled through C&EN. This discussion focused on the importance of the structural distortion and bond lengths of the Al_4^{4-} framework in Li_3Al_4^- , relative to cyclobutadiene, in indicating aromatic and antiaromatic behavior. Other topics of discussion focused on interpreting the electron energies of Li_3Al_4^- determined by photoelectron spectroscopy, whether NICS values were consistent with the nature of the molecular orbitals or can properly be

used as a probe for σ aromaticity, and how the 3s Al lone pairs figure into the net chemical bonding.

"We appreciate Schleyer, Chen, and coworkers' interest in the new all-metal aromatic and antiaromatic molecules and their contribution to the discussion of the chemical bonding in these systems," Boldyrev and Wang note. "These molecules have major differences from aromatic hydrocarbons because they usually exhibit multiple aromatic and antiaromatic properties. We expect that this discussion will continue and should help achieve a deeper understanding of these novel molecular systems."

"While we appreciate this conciliatory statement," Schleyer replies, "we do not agree that there are 'major differences.' As shown in our papers, the magnetic behavior of the benzene σ system opposes the π . This is the reverse of the situation in Li_3Al_4^- . We see no fundamental differences between metal, main-group, and organic systems, other than those based on variations of the numbers of valence electrons and occupied MOs.

"We also would like to emphasize that there is nothing 'metallic' about small aluminum clusters," Schleyer continues. "These behave like clusters of boron, granting the usual differences between the rows of the periodic table. Many more atoms are needed before clusters of aluminum and other electropositive elements exhibit metallic behavior. Boldyrev and Wang's 'all-metal antiaromatic' claim is misleading, as the molecule is just made up of main-group elements."

Boldyrev responds: "One can argue about how many atoms of an element are required for metal behavior, but the characterization of aluminum as a metal is undeniable."

Schleyer also makes a point that Li_3Al_4^- would not be the first all-metal antiaromatic compound. "There are true antiaromatic all-metal clusters, such as Sn_6^{2-} prepared in the solid phase a decade ago, which have escaped recognition," he says. Boldyrev and Wang are in the process of examining Sn_6^{2-} and related octahedral clusters, they say. They believe that perfectly octahedral structures such as Sn_6^{2-} cannot be antiaromatic.

So, whom should one believe in this standoff?

C&EN asked chemistry professor [Patrick W. Fowler](#) of the University of Exeter, in England, to weigh in on the debate. Fowler and his coworkers have just published a paper that examines the aromaticity and antiaromaticity in Li_xAl_4 compounds. "This debate hinges on two different definitions of aromaticity and antiaromaticity that agree in simple cyclic carbon compounds but do not always agree elsewhere," he says.

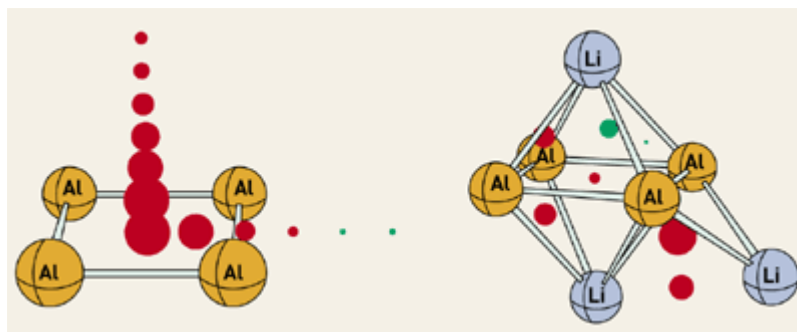
Fowler agrees with Schleyer and Chen that counting π electrons alone is not good enough evidence to decide whether the all-metal clusters are aromatic or antiaromatic. For example, benzene with six π electrons is energetically, chemically, and magnetically aromatic, he says, whereas cyclobutadiene with four π electrons is undisputedly antiaromatic. "But simple counting can sometimes mislead. Borazine ($\text{B}_3\text{N}_3\text{H}_6$) has six π

electrons, but it's not aromatic, for example."

Fowler and his coworkers previously demonstrated that the induced ring current in Al_4^{2-} is essentially a σ -bonding effect, with little or no contribution from the π electrons. In their new paper, they computed magnetic-field-induced current-density maps of the 2π systems in LiAl_4^{2-} and Li_2Al_4 and 4π systems in Li_3Al_4^- and Li_4Al_4 [*Phys. Chem. Chem. Phys.*, published online, <http://www.rsc.org/is/journals/j1.htm> (DOI: 10.1039/b311559n)]. They used an "ipsocentric" method that, like NICS, allows the electron current density to be partitioned into the π and σ MO contributions.

Although NICS is an indirect theoretical probe of the currents, Fowler notes, the ipsocentric mapping approach gives a direct answer to the question of aromaticity and antiaromaticity based on the magnetic criterion. The density maps show that all four compounds sustain a diatropic (aromatic) σ ring current in the plane of the Al_4 unit, Fowler says. In the 2π systems, despite the Hückel count for aromaticity, the π orbital is magnetically inactive, or atropic, with no ring current observed above the plane of the ring. They attribute the lack of the π magnetic activity to the lack of overlap of the π orbital with empty orbitals of suitable symmetry. Thus, the conclusion is that the σ aromaticity dominates.

The Li_3Al_4^- 4π system, on the other hand, has a paratropic (antiaromatic) π current above the plane. The question of aromaticity and antiaromaticity is thus complicated for these species by cancellation of the currents, Fowler notes. "The best description of this species is σ aromatic and π antiaromatic. The balance depends on where the molecule is probed. Above the Al_4 plane, the current in Li_3Al_4^- is purely paratropic." Thus, Fowler's description comes down squarely as being neutral in the debate.



DIAMAGNETIC VIEW Schleyer and Chen's nucleus-independent chemical shift (NICS) method provides an indirect theoretical probe of ring currents to provide "absolute magnetic shielding" and serves as a definitive measure of aromaticity and antiaromaticity. In the plotted data shown for Al_4^{2-} (as in LiAl_4^-) and Li_3Al_4^- , red circles represent diamagnetic (aromatic) regions, and green circles represent paramagnetic (antiaromatic) regions. The NICS data indicate that in most regions of the molecules, diamagnetism prevails and that LiAl_4^- and Li_3Al_4^- should both be considered aromatic.

OTHER CONTRIBUTORS to the discussion include chemistry professors [Sason Shaik](#) of Hebrew University of Jerusalem, in Israel, and [Philippe C. Hiberty](#) of the University of Paris South, in France. "The molecules addressed by Boldyrev and Wang and by Schleyer and Chen are beautiful--if intellectual beauty counts--since these species demonstrate the choice of bonding motifs made by different elements in the periodic table," they tell C&EN.

Shaik and Hiberty addressed this general bonding issue in the early 1980s, showing that for strong binders like carbon and nitrogen, π electrons will be fully delocalized only if the σ frame has a strong enough force constant to restrain the "distortive" π electrons [[Chem. Rev.](#), **101**, 1501 (2002)]. "When this occurs, as in benzene, the π electrons are both distortive and delocalized, and hence they will exhibit aromatic NICS and at the same time reveal the inherent π distortivity," they note.

Shaik and Hiberty further predicted that the chances of finding truly delocalized antiaromatic or aromatic compounds with σ and π subsystems are greatest with weak binders, such as the metallic elements discussed in this debate or, in general, elements in the lower part of the periodic table. In this respect, it's "remarkable" that Li_3Al_4^- , which they agree should be considered net aromatic, is still a bit distortive. "This shows that the inherent distortivity is still there," they say.

However, after calculating the bonding in the Li_3Al_4^- species without the Li^+ ions, Shaik and Hiberty observe a completely different electronic structure: "The π system now has only two electrons and is aromatic, while the σ system gains a bonding electron pair. The Li^+ ions drive the electronic structure to be what it is. In any event, the realization of such all-metal species is an exciting development, because it will eventually lead to a general theory of electronic conjugation, not one that is restricted to carbon chemistry," they conclude.

Another contributor to the discussion is senior research scientist [Dage Sundholm](#) of the department of chemistry at the University of Helsinki, in Finland. Sundholm's group has published several papers that explore aromaticity and antiaromaticity, including one on Al_4^{22} compounds. After reading Schleyer's paper, Sundholm began a computational study to compare the aromaticity in Al_4^{2-} and Al_4^{4+} , and his group is currently preparing to submit a paper.

Sundholm has developed aromatic ring-current shielding (ARCS), a slightly different method to calculate NICS points. In Sundholm's approach, long-range magnetic shielding is calculated along a perpendicular line extending down a symmetry axis of the ring. The idea is that a ring current gives rise to a magnetic shielding far away from the molecule. Sundholm finds that, similar to NICS, the magnetic shielding calculated by ARCS at the center of the Al_4^{4+} ring is diatropic. But at distances farther away from the center, the shielding is paratropic.

"The normally reliable NICS calculations fail in this case," Sundholm says, "probably because of the smaller ring size over traditional organic compounds and perhaps also because of confinement of the ring by the lithium ions. The ARCS calculations provide additional information

about the induced ring currents, but the ultimate computational method for determining the degree of molecular aromaticity has not yet been invented."

Schleyer is quick to point out that he believes the σ ring current effects fall off away from rings much more rapidly than do π effects. "Hence, Sundholm's remote sampling point only picks up the π effect, and cannot measure the total aromaticity of the molecule." Sundholm counters that he thinks the σ and π currents obey the same physics, and that, either way, a mathematical proof could provide the answer.

Although the debate over aromaticity-antiaromaticity in these all-metal systems is yet to be resolved, the understanding to be gained will likely inspire the study of other tantalizing inorganic cluster compounds. These include planar B_8 and B_9 "molecular wheels" being explored by Boldyrev, Wang, and their colleagues and "spherical" aromatics such as Li_2Ge_8 and other cage compounds being explored by Schleyer, Chen, and their colleagues.

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