

Aromaticity in inorganic chemistry: the Hückel and Hirsch rules

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Aromaticity is an important idea in organic chemistry,¹ enabling us to classify empirical data, rationalize chemical bonding, and predict stability and reactivity of thousands of organic compounds. Aromaticity is a manifestation of multicentered bonds in closed circuits.² It is a shortcut for describing a series of physical properties that cannot be accommodated within the concept of two-centered/two electron bonds, such as high enthalpies of formation, intermediate bond lengths, and ring current resulting in shielding of NMR signals.² Chemically, aromaticity is associated with low reactivity and, if applicable, substitutions, instead of additions.²

It is logical to ask if aromaticity is also a useful notion in inorganic chemistry. Analysis of the literature suggests that aromaticity allows one to justify or even predict stability and reactivity of inorganic species, and guides the design of new materials. Whereas organic compounds need to be planar to be aromatic, no such limitation applies to inorganics. An inorganic compound may be expected to be aromatic if it satisfies a “counting rule”; the familiar Hückel rule applies to planar aromatics and the Hirsch rule works for spherical analogs^{3,4}.

Probably the most celebrated examples of aromatic inorganic compounds are fullerenes, boranes and carboranes.³ Significant downfield chemical shifts of ³He encapsulated in fullerenes is a common marker of their aromaticity. These fullerenes satisfy the Hirsch rule, which postulates a special stability (i.e., aromaticity) of spherical systems with $2(n+1)^2$ valence electrons.⁵ It is best illustrated by an I_h fullerene, whose nearly spherical valence shells resemble those of an isolated atom with its *s*, *p*, *d*, *f*, etc. atomic orbitals (Figure 1).⁵ The Hirsch rule works equally well for a variety of inorganic cage molecules, including boranes and carboranes.⁶ For example, electron delocalization results in carborane anions being remarkably poor nucleophiles. This fact has been exploited by C. Reed to construct “ideal” superacids, enabling him to isolate a number of protonated intermediates as stable species in the solid state (Figure 2) and helping to understand the acid-catalyzed reaction mechanisms.⁷⁻⁹ The Hirsch rule has also predicted the existence of aromatic Au₃₂ and Au₅₀ clusters,^{10,11} anticipating their experimental confirmation and pharmaceutical applications.

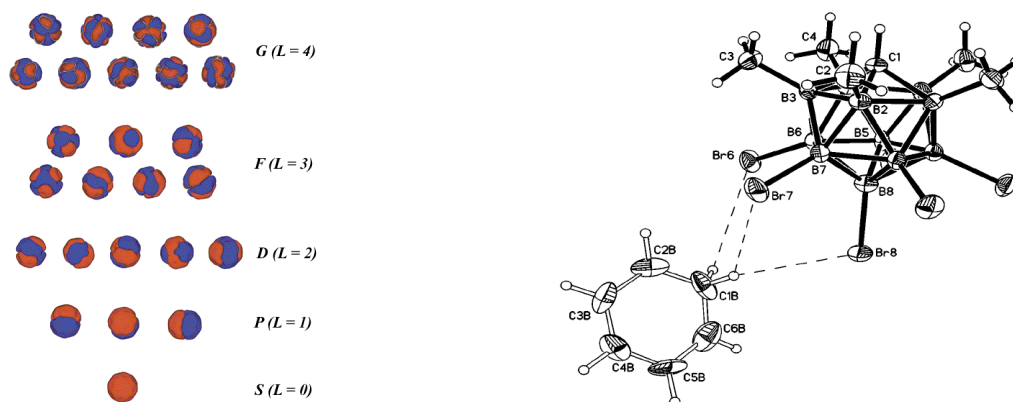


Figure 1: π MO orbitals of C_{60}^{10+} .⁵ **Figure 2:** X-ray structure of benzenium ion stabilized by the carborane anion $[CB_{11}HMe_5Br_6]^-$.⁸

In planar compounds, the closed shell electronic structure is achieved with $4n+2$ electrons, in accord with the familiar Hückel rule of aromaticity. Metallabenzenes,¹² where the $d\pi$ - $p\pi$ interactions lead to closed-shell population, exhibit aromaticity and undergo electrophilic substitutions¹³. The notion of aromaticity allows us to justify the unusual stability of $R_3Ga_3^{2-}$ in $Na_2[(Mes)_2C_6H_3]Ga_3$ (Mes = 2,4,6-Me₃C₆H₂), as it is isoelectronic with a classical organic aromatic compound, $C_3H_3^+$.^{14,15} The Hg_4^{6-} square anion is abundant in Na-Hg amalgams.¹⁶ Although bonding in Hg_4^{6-} has been difficult to fully understand, an isoelectronic species, Al_4^{2-} , has been prepared in the gas phase and studied by photoelectron spectroscopy and high level computations.^{17,18} Its π aromaticity is consistent with the Hückel rule from the electronic structure analysis (Figure 3),¹⁹⁻²¹ and is supported by the computed stability of all-metal analog of metallocenes²². Knowledge of antiaromaticity also enables us to rationalize the rectangular geometry of the $2e^-$ reduced species, Al_4^{4-} ,^{20,23} and its stabilization upon coordination to transition metals, similar to cyclobutadiene, a typical organic antiaromatic compound.²⁴

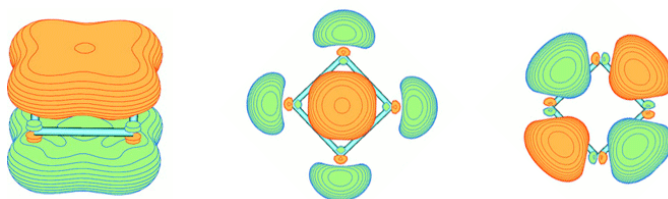


Figure 3: The highest three occupied MO orbitals of Al_4^{2-} . From left to right: HOMO (π), HOMO-1 (\square), HOMO-2 (\square).¹⁷

Extending the idea of aromaticity into inorganic chemistry has stimulated the synthesis of several novel species and the development of inorganic analogs of organic aromatic substitution reactions, and aided in the design of new materials. The idea of aromaticity would continue to motivate and guide synthetic inorganic chemists.

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