

An Aromaticity Scale Based on the Topological Analysis of the Electron Localization Function Including σ and π Contributions

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Abstract: In this work, the average bifurcation value of the electron localization function (ELF) of both σ (ELF σ) and π (ELF π) contributions was used to construct an aromaticity scale for chemical compounds. We have validated the scale with a series of well-known molecules and then used it to evaluate global aromaticity on aluminum based clusters, which present σ aromaticity and π antiaromaticity. The proposed scaled predicts an overall antiaromatic character for the Al_4^{4-} moiety.

Introduction

The concept of aromaticity and, by extension, antiaromaticity, has general acceptance among the chemical community. However, the criteria used to validate the aromaticity or antiaromaticity of a chemical compound are controversial,^{1–8} due to the fact that a well-established definition of these concepts has yet to be presented in a quantitative way for general use.^{2–21}

Currently there is an interesting discussion about the net aromaticity of a chemical species when it presents both, σ aromaticity and π antiaromaticity.²² The all metal cluster Al_4^{4-} is a classical example where this phenomenon appears to be present. The Al_4^{4-} ring in Li_3Al_4^- is not square. It has two slightly different bond lengths, and it contains 4π electrons. These characteristics plus the shape of the molecular orbitals have been used to classify this species as antiaromatic.²³ On the other hand however, this analysis has been presented as an incomplete view of the electronic properties of this compound, because, although the cluster is π antiaromatic, it presents characteristics of aromaticity in its σ system.²⁴ While the different studies^{23,24} agree in the σ aromatic and π antiaromatic character of the ion, the

differences appear in the global characterization of the species as aromatic or antiaromatic.

The lack of a unique scale of aromaticity is an important limiting factor in this debate. Scales based on structure or energetic behavior such as the harmonic oscillator model of aromaticity (HOMA)^{25,26} or the aromatic stabilization energy (ASE),² respectively, have been proposed. Other aromaticity criteria based on the analysis of electron delocalization^{12,13} or associated to measurable response properties²⁰ have also been used. These scales have been constructed thinking in traditional organic aromatic rings, and it is not clear that they can be applied to all metal clusters. Recently, the nucleus independent chemical shift (NICS) index,⁵ based on magnetic properties, has been extensively used in the theoretical literature. Extensions and modifications^{5,6} as well as criticism^{16,19} of this methodology have been published.

An alternative approach, based on properties of the electron density probed by the electron localization function (ELF)²⁷ of Becke and Edgecombe,²⁸ has been introduced to understand aromaticity.^{14,15,29} A separation of the ELF into its σ and π components was shown to provide a useful scheme to discuss σ and π character in a molecular system.³⁰ The ELF is defined in terms of the excess of local kinetic energy density due to the Pauli exclusion principle, $T(\rho(r))$, and the Thomas-Fermi kinetic energy density, $T_h(\rho(r))$

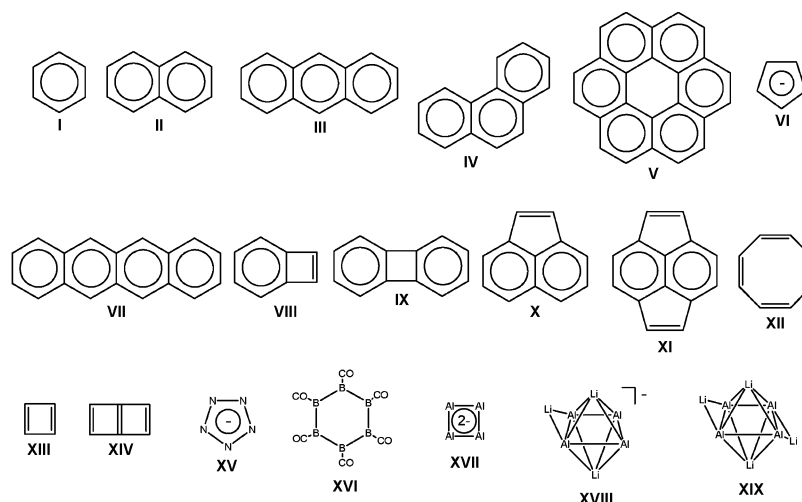
$$\text{ELF} = \left[1 + \left(\frac{T(r)}{T_h(r)} \right)^2 \right]^{-1}$$

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Chart 1. Molecules Analyzed

Its numerical values are conveniently mapped on the interval (0,1) facilitating its analysis and interpretation. According to the interpretation of the ELF, a region of the space with a high value of ELF corresponds to a region where it is more probable to localize an electron or a pair of electrons. Hence, local maximum (attractors) of the ELF characterize these regions, and the volume enclosed by all gradient lines which end up at one attractor is called a basin. At low values of the ELF, the volume enclosed by the respective isosurface may contain more than one attractor, and eventually, for a sufficiently low value, all the attractors will be contained in the isosurface. When the isosurface goes to larger values of the ELF, the basins begin to split, and, finally, the respective isosurface shows all the basins separated. This process is conveniently followed by means of a bifurcation diagram.³¹ The bifurcation points have been interpreted as a measure of the interaction among the different basins and, chemically, as a measure of electron delocalization.^{31,32} Here, this scheme will be used to construct a σ and π aromaticity scale. This scale will be validated with a series of well-known molecules (**I–XIV**) and two recently proposed aromatic molecules N_5^- (**XV**)³³ and B_6CO_6 (**XVI**)³⁴ and then used on the new aluminum based clusters, **XVII**, whose aromatic properties have recently been described,^{35–38} and **XVIII** and **XIX** where the net aromaticity of both systems has been a matter of recent controversy.^{22–24}

We will show that the average between the two bifurcation values provides a useful measure of the global aromatic character of a molecular system.

Computational Details

The molecules in Chart 1 have been studied. All molecular geometries were optimized at the B3LYP/6-31G(d) level of theory using the GAUSSIAN98³⁹ package of programs. The π and σ orbitals were separated to form the π and σ densities, respectively. The separated ELF, ELF_π , and the ELF_σ , were constructed using the TopMod⁴⁰ software. The visualization of the isosurfaces and the bifurcation points were done using the Vis5d⁴¹ program.

Results and Discussion

The σ – π separation of the ELF rest upon the additive character of the kinetic energy and reflects the symmetry

Table 1. Bifurcation Values of ELF_σ and ELF_π and Their Average for All Molecules Analyzed^a

molecules	ELF_σ	ELF_π	average
I	0.76	0.91	0.84
II	0.76	0.78	0.77
III	0.77	0.70	0.74
IV	0.75	0.64	0.70
V	0.76	0.75	0.76
VI	0.75	0.82	0.79
VII	0.74	0.69	0.72
VIII	0.76	0.72	0.74
IX	0.76	0.74	0.75
X	0.76	0.75	0.76
XI	0.77	0.71	0.74
XII	0.73	0.35	0.54
XIII	0.79	0.11	0.45
XIV	0.78	0.15	0.47
XV	0.81	0.78	0.80
XVI	0.68	0.85	0.77
XVII	0.88	0.99	0.94
XVIII	0.86	0.08	0.47
XVIII	0.86	0.41	0.64
XIX	0.87	0.24	0.56

^a The two ELF_π bifurcation values of compound XVIII correspond to the separation of the basins over and under the plane of the Al_4 ring, respectively.

properties of the molecular system. It is expected that the main characteristics of the π cloud should be reflected in the ELF_π . In particular, a high value of bifurcation implies that the minimum in the ELF is high and the respective basins do not separate each other. Therefore, in this situation the basins are correlated, and one can expect that the higher the bifurcation value the more aromatic the system will be.

Table 1 displays the bifurcation ELF_σ and ELF_π values and their average for all the molecules considered in this study. There are some clear trends worth commenting. For the traditional π aromatic molecules (**I** to **XI**), the sigma bifurcation occurs at ELF_σ values around 0.75 with small deviations, and the ELF_π bifurcation values correspond perfectly with the aromatic degree of the molecular systems as was previously discussed.²¹ Notice that the antiaromatic molecules (**XII** to **XIV**) have a remarkable low bifurcation

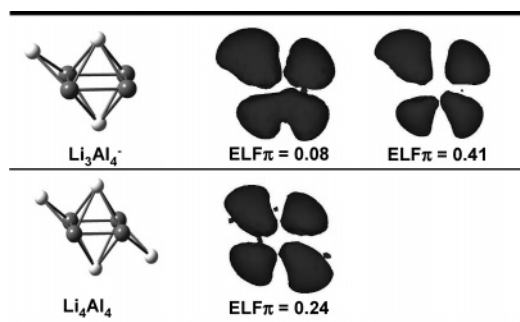


Figure 1. π System bifurcation of the Al_4^{4-} ring in Li_3Al_4^- and Li_4Al_4 .

ELF_π value. On the other hand, the metallic systems (**XVIII** and **XIX**) and the N_5^- ion (**XV**) present a high value of the bifurcation ELF_σ which is related to their σ aromaticity. For the last systems, the ELF_π bifurcation values show great variations thereby reflecting the fact that some of them are π antiaromatic (**XVIII** and **XIX**). The opposite character of the π and σ parts of the Li_3Al_4^- and Li_4Al_4 metallic systems has raised the question about the global aromatic or antiaromatic character of these clusters. In an attempt to bring a new perspective to the point, the average value of the two bifurcations for each molecule has been calculated. They are displayed in the third column of Table 1. For the classic organic compounds, one can clearly observe that the aromatic molecules present values higher than 0.70 (**I** to **XI**), and the antiaromatic ones have values around 0.55 or lower (**XII** to **XIV**).

Using this range of values to classify the new systems, **XV**, **XVI**, and **XVII** are clearly aromatic. The situation is different for the Li_3Al_4^- ion (**XVIII**). It presents two different types of ELF_π bifurcation as can be seen in Figure 1. The first bifurcation (0.08) corresponds to the separation of the basins over the plane of the ring, and the other bifurcation (0.41) is associated with the separation of the basins under the plane of the ring. This is surely due to the asymmetric capping of the lithium atom. Depending on which value one takes, the average is 0.47 or 0.64. In both cases, the molecule does not enter into the category of aromatic in the proposed scale. However, to provide additional evidence, the symmetric Li_4Al_4 cluster (**XIX**) has also been studied. The ELF_π bifurcation is now well defined, as can be seen in Figure 1, and has a low value of 0.24. The ELF_σ bifurcation occurs at a value of 0.87, and the average is 0.56, similar to the value obtained for cyclooctatetraene (**XII**), an antiaromatic molecule. It is interesting to note that this value is similar to the average between the two bifurcation values for the Li_3Al_4^- ion (**XVIII**).

Conclusions

The average value of the ELF_σ and ELF_π bifurcations can be used to construct a general scale to measure the aromaticity of a molecular system. It works well for known organic and metallic aromatic and antiaromatic systems. The proposed scale predicts an overall antiaromatic character for the controversial Al_4^{4-} -based clusters, built from σ aromatic and π antiaromatic contributions.

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