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Is Al_2Cl_6 Aromatic? Cautions in Superficial NICS Interpretation

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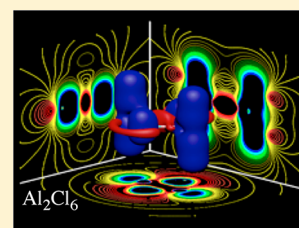
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ABSTRACT: In this article, we employed the induced magnetic field method to show that the Al_2X_6 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) clusters cannot be classified as aromatic systems. Interestingly, even nucleus independent chemical shift (NICS) reveals the same conclusion when analyzed in greater detail, showing that a superficial analysis of this index can easily lead to incorrect interpretations. In view of the fact that the NICS index is extensively used by computational and theoretically oriented experimental chemists, this is an important warning against superficial analyses, as it can lead to erroneous chemical interpretation.



INTRODUCTION

Quite recently, Nori-Shargh et al.¹ claimed that Al_2X_6 compounds ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) should be considered as σ -aromatic based on nucleus independent chemical shift (NICS) computations,² one of the most popular tools for diagnosing aromaticity.³ The NICS value at the center of the Al_2X_2 quadrangle is -7.0 ppm for Al_2F_6 and monotonically decreases down to -3.5 ppm for Al_2I_6 . These small NICS values and the nature of these systems caught our attention because their classification of these compounds as aromatic could instead be due to improper NICS interpretation.

NICS is defined as the negative value of the absolute shielding computed at the ring center of a molecule (or at some other point, usually at 1 Å). Rings with large negative NICS values are generally classified as aromatic, whereas positive values are associated as a symptom of antiaromaticity.³ The main advantage of NICS is its accessibility because it is commonly implemented in standard packages. However, this index is not free of controversy. Several authors have pointed out that diamagnetic ring currents are limited by the potential spurious contribution from in-plane tensor components that are not related to aromaticity.^{4–10}

Even though aromaticity is not rigorously well-defined and was originally developed within the organic chemistry scheme, this useful concept has since been extended to inorganic systems as well.^{11,12} Interestingly, some all-metal clusters and inorganic compounds possess not only the conventional π -(anti)aromaticity but also the σ -, δ -, or even ϕ -(anti)-aromaticity, i.e., multifold aromaticity.¹³ However, the extrapolation of the aromaticity notion from the organic to the inorganic world should be done cautiously in order to avoid abuse of this already fuzzy concept.

In this article, we analyzed in detail the electron delocalization of the title systems using another magnetic

descriptor: the induced magnetic field.^{14–16} The induced magnetic field reveals important information on electron delocalization and, furthermore, of its origin. In agreement with current density maps, the response of aromatic, antiaromatic, and nonaromatic examples define qualitatively and quantitatively different features. Particularly, the z -component of the induced magnetic field (B_z^{ind}), which is equivalent to NICS_{zz} , includes only the out-of-plane response. We found that, by using B_z^{ind} , the Al_2X_6 systems cannot be classified as aromatic; interestingly, even NICS reveals the same conclusion when it is analyzed in greater detail, showing that a superficial analysis of this index could easily be derived by wrong interpretation. Put more simply, even though the NICS values are negative at the center of the Al_2X_2 rings, the Al_2X_6 cannot necessarily be classified as aromatic.

COMPUTATIONAL DETAILS

The geometry optimizations and the induced magnetic field (B^{ind}) computations were performed with the Perdew–Wang 91 functional (PW91)¹⁷ in the Gaussian09 program,¹⁸ in conjunction with the def2-TZVP basis set.¹⁹ The shielding tensors were computed using the GIAO approach. Induced magnetic fields of the external field applied perpendicularly to the molecular plane were computed in ppm. Assuming an external magnetic field of $|B^{\text{ext}}| = 1.0$ T, the unit of B^{ind} is 1.0 μT , which is equivalent to 1.0 ppm of the shielding tensor. In order to render the induced magnetic fields, the molecules were oriented so that the center of mass was located at the origin of the coordinate system; the z -axis is concurrent with the highest

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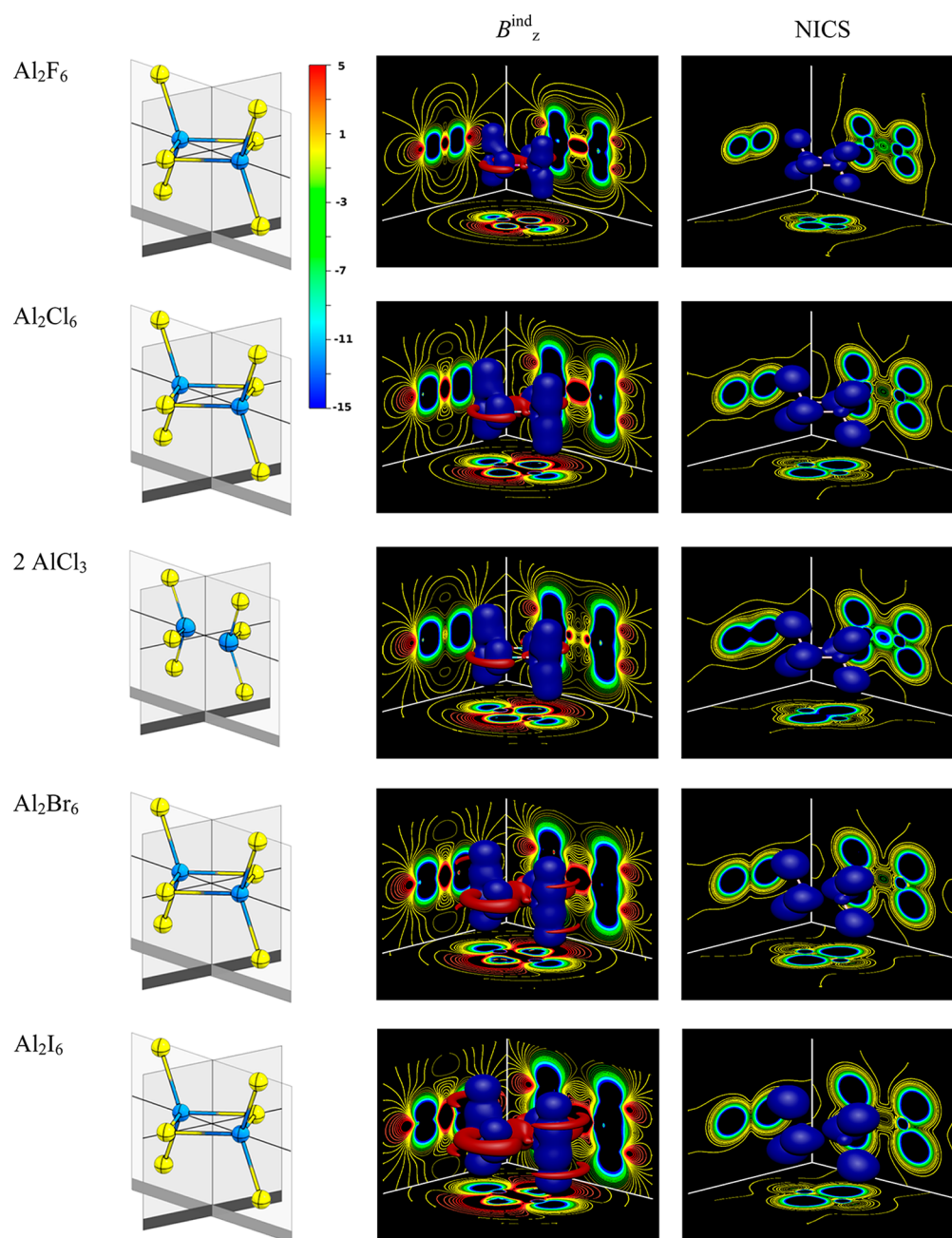


Figure 1. Isosurfaces and the contour lines, in the molecular plane and perpendicular to the molecular plane through the origin, of the z -component of the induced magnetic field (B_z^{ind}) and NICS at $5.0 \mu\text{T}$ and $-15.0 \mu\text{T}$ for the Al_2X_6 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) complexes. Blue and red indicate shielding (negative values) and deshielding (positive values), respectively. The scale is given in ppm.

order symmetry axis of the molecule. The external field was applied perpendicular to the Al_2X_6 quadrangle.

To gain further insight on the electron distribution, the adaptive natural density partitioning (AdNDP),²⁰ developed by the group of Boldyrev, was done. The results of the AdNDP analysis were obtained at the PW91/def2-TZVP level.

■ INDUCED MAGNETIC FIELD ANALYSIS

Figure 1 depicts the contour lines and isosurfaces of both the z -component of the induced magnetic field, B_z^{ind} , and the NICS for Al_2X_6 . It is important to remark again that B_z^{ind} for an external field perpendicular to the ring is equivalent to the NICS_{zz} index.²¹ In the case of the Al_2X_6 complexes, B_z^{ind} shows a paratropic region (shown in red) with values ranging from

+14.4 ppm (Al_2F_6) to +22.6 (Al_2I_6) at the ring center. This is in contrast to the NICS field, which presents only a weak and very short-range, and localized diatropic region (given in blue) inside the ring and the deshielding regions are further outside. For comparison, in a typical aromatic molecule, like benzene, a long-range diatropic cone is perceived above and below the ring for both magnetic descriptors (NICS and B_z^{ind}) (see Figure 2).

Perhaps it is not fair to compare the Al_2X_6 magnetic response to that of benzene because the Al_2X_6 compounds were classified as σ -aromatic by Nori-Shargh et al.¹ However, H_3^+ and C_3H_6 , which have been classified as σ -aromatic systems, although there is still a controversy around cyclopropane,^{5,22} show also a strongly diatropic induced magnetic field and long-range response inside the ring (see Figure 2). Notice that the shape

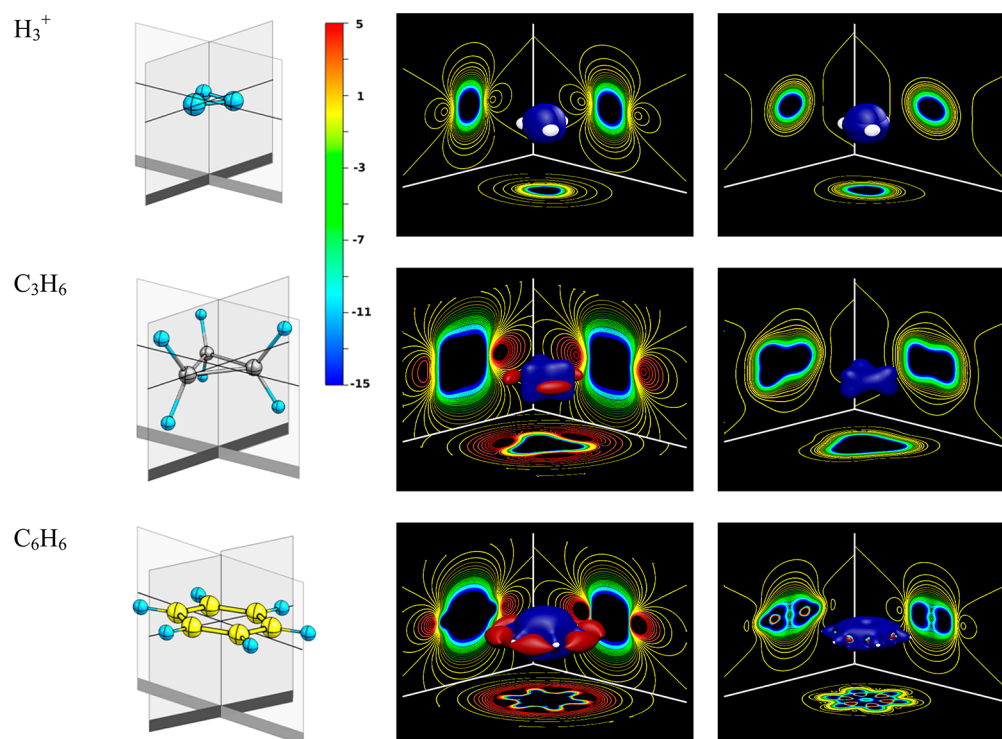


Figure 2. Isosurfaces of the z -component of the induced magnetic field (B_z^{ind}) and NICS at $5.0 \mu\text{T}$ and $-15.0 \mu\text{T}$ for H_3^+ , benzene, and cyclopropane. See Figure 1 for more computational details.

and intensity of the magnetic response of benzene, H_3^+ , C_3H_6 , and Al_2X_6 are absolutely different. So, the title systems cannot be classified as aromatic ones, sigma or otherwise.

NICS, defined as the negative total isotropic shielding (average shielding), can be computed at any point in space. Isolines and isosurface of NICS, that is, the effect on the isotropic shielding, caused by external magnetic fields from all directions, are also depicted in Figure 1. The average shielding evaluated at the ring center of the Al_2X_6 complexes corresponds to a NICS index as is reported in Table 1 (cf. Nori-Shargh et

Table 1. z -Component of the Induced Magnetic Field (B_z^{ind}) and NICS in ppm, Computed at the Ring Center and 1.0 \AA above the Ring

system	NICS (0)	B_z^{ind} (0)	NICS (1)	B_z^{ind} (0)
Al_2F_6	−7.3	14.4	−2.1	−1.1
Al_2Cl_6	−5.1	17.1	−1.5	4.1
Al_2Br_6	−4.6	20.1	−1.3	6.3
Al_2I_6	−3.8	22.6	−0.9	8.9
H_3^+	−33.4	−37.0	−2.2	−8.0
C_3H_6	−43.8	−32.0	−8.6	−24.4
C_6H_6	−7.9	−15.9	−9.8	−29.5
AlF_3	−9.3	−1.1	−2.4	−3.2
AlCl_3	−8.3	−0.4	−2.9	−1.9
AlBr_3	−8.2	0.4	−3.1	−1.4
AlI_3	−8.2	0.54	−3.4	−1.0

al.¹). The large anisotropies of the shielding tensors of the Al_2X_6 complex lead to significant change between both B_z^{ind} and NICS scalar fields: (1) the isotropic shielding is smaller in magnitude than that caused only by an external field in the z -direction; (2) close to the ring center the NICS values are negative showing a low diatropic character. In benzene, the

absolute value of the $(\sigma_{xx} + \sigma_{yy})$ term is smaller than the σ_{zz} one; therefore, the B_z^{ind} and NICS have the same sign. In the case of the Al_2X_6 compounds, the NICS tensor is strongly anisotropic at the ring center, giving a large difference between both aromaticity indexes. However, again, in order to classify a molecule as aromatic, it is not only mandatory to compute the magnetic response just at the ring center (this is the main reason why NICS(1) was originally suggested as an alternative index)²³ but also quite important to figure the shape and intensity of the cones.

Let us consider the notion for a moment that the Al_2X_6 complexes are aromatic. If true, the magnetic response provided by two free AlCl_3 fragments (geometrically deformed from their equilibrium geometry to their geometries in the Al_2Cl_6 complex) should be less diatropic to that obtained for Al_2Cl_6 . However, it can be seen in Figure 1 that this is clearly not the case. Interestingly, while at the ring center the contribution of each fragment to B_z^{ind} is just -0.4 ppm , (i.e., the sum of the two fragments is -0.8 ppm), lower than that of the complex (17.1 ppm). Of course, this approximation is valid only in those cases where the interaction energy between two fragments is small. In this sense, our results provide evidence that the noninteracting AlCl_3 dimer is more diatropic (i.e., more aromatic) than Al_2Cl_6 . Similar conclusion can be emerged from the NICS analysis when carefully examined.

■ ADAPTIVE NATURAL DENSITY PARTITIONING ANALYSIS

In principle, we would like to find delocalized orbitals in a putative aromatic system like in benzene. This is our first indicator of electron delocalization, with others. In order to check for potential electron delocalization, we employed the adaptive natural density partitioning (AdNDP) method.²⁰ The AdNDP analysis is based on the concept of an electron pair as

the main chemical bonding element. It represents the electronic structure in terms of n -center two-electron ($nc-2e$) bonds. The n values range from one to the total number of atoms in a molecule. So, AdNDP recovers both Lewis bonding elements ($1c-2e$ or $2c-2e$ objects) and delocalized $nc-2e$ bonds ($n > 2$), which are associated with the aromaticity concept. The AdNDP analysis revealed eight $2c-2e$ σ -bonds with occupation number (ON) in the range of 1.95–2.00 lel (see Figure 3). The

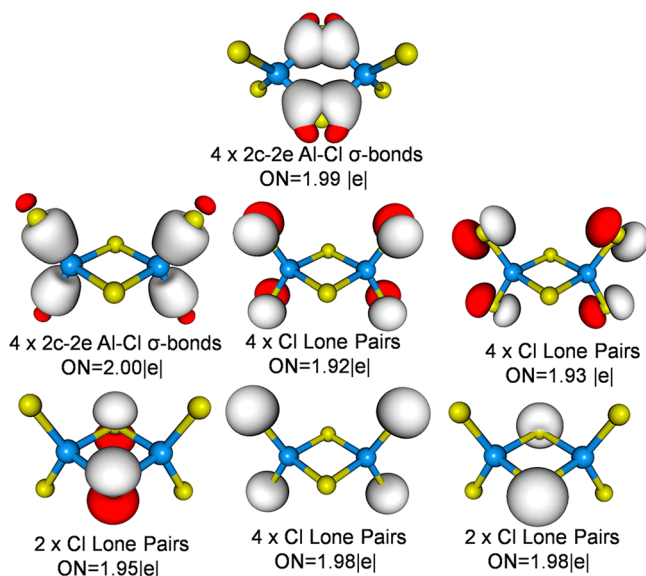


Figure 3. AdNDP bonding pattern analysis for Al_2Cl_6 at PW91/def2-TZVP level.

AdNDP also reveals three lone pairs for each peripheral chlorine atom and two lone pairs for the bridging Cl, recovering the classical bonding picture for the Al_2X_6 complexes. No single multicenter bonding was found, indicating that the Al_2X_6 complexes cannot be considered as aromatic systems, in line with the magnetic response reasoning above.

In conclusion, not all that has a negative NICS is aromatic. In order to classify a molecule as aromatic, it is mandatory not only to compute the magnetic response just at the ring center, it is also quite important to figure the shape and intensity of the magnetic response. Our results show the clear limitation of the NICS index when a strong anisotropy is exhibited. In view of the fact that the NICS index is extensively used by computational and theoretically oriented experimental chemists, this is an important warning. This is not to say that NICS is not a useful tool to diagnose aromaticity, but like any method, NICS has limitations, which are important to take into account.

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Notes

The authors declare no competing financial interest.

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