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Journal:	<i>Chemical Society Reviews</i>
Manuscript ID:	CS-TRV-02-2015-000114.R2
Article Type:	Review Article
Date Submitted by the Author:	10-May-2015
Complete List of Authors:	Stanger, Amnon; Technion, Chemistry Gershno-Poranne, Renana; Technion, Chemistry

Magnetic Criteria of Aromaticity

Renana Gershoni-Poranne^[a] and Amnon Stanger^{*[a]}

Addresses

[a] R. Gershoni-Poranne, Prof. A. Stanger

Schulich Faculty of Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry,
Technion – Israel Institute of Technology, Haifa 32000, Israel.

E-mail: stanger@technion.ac.il

Dedication

Dedicated to Prof. Yitzhak Apeloig on the occasion of his 70th birthday.

Introduction

Preface: Benzene was discovered in 1825 by Faraday. The determination and understanding of its structure presented a great challenge to scientists: the compound was highly unsaturated, yet did not show any of the typical reactions of unsaturated compounds, e.g., addition of bromine. The first suggestion that the molecule is cyclic is traditionally attributed to Kekulé in his 1865¹ and 1866² papers, although some argue that this idea was presented earlier by Josef Loschmidt.³ In any event, accumulating experimental evidences, mainly experiments that were conducted by Ladenburg and Wroblewsky, indicated that the proposed structure was unsatisfactory, as it did not account for there being only three disubstituted isomers of benzene instead of the expected four. It was only in 1872 that Kekulé suggested oscillating structures, in which synchronous 1,2-shifts of the three double bonds occur very rapidly.⁴ It took about six decades until Erich Hückel⁵⁻⁹ and Linus Pauling¹⁰ introduced their quantum mechanical based MO and VB explanations, respectively, which introduced the concept of delocalization (of bonds and electrons). This fundamental property is vital to the topic of the present paper.

When a metallic loop (containing delocalized electrons) is inserted into a magnetic field, an electric current is induced. The current in the loop induces a magnetic field that opposes the external magnetic field at the inside of the loop. Aromatic molecules contain cyclically delocalized electrons and therefore, when subjected to a magnetic field, show a ring current and a resulting induced magnetic field. However, there are some fundamental differences between the classic (loop) and quantum (molecular) phenomena. The main one, which is relevant to this paper, is the direction (sense) of the induced current and its resulting induced magnetic field. While the direction of an induced current in a loop is determined by the relative orientation of the magnetic field and the loop's movement, the direction of the current in a molecule depends also on the type of the system. Generally, an external magnetic field

induces a paratropic ring current (the opposite direction relative to a classic loop) in a system that contains $4n$ π electron, while a system containing $(4n+2)$ π electrons shows a diatropic ring current (the same direction as a classic loop). A frontier orbitals based explanation has been offered by Fowler and collaborators.¹¹⁻¹³ In a nutshell, this explanation rests on the different symmetry changes that take place when, under an external magnetic field, a HOMO-LUMO transition occurs in the double-degenerated HOMO of a $(4n+2)$ π electrons system to the doubly degenerated LUMO vs. a single HOMO to a single LUMO level in $4n$ π electrons systems. This, in turn, causes a different balance between the linear momenta of transition, which produce diatropic ring currents, and angular momenta of transition, which produce paratropic ring currents. A later work by Corminboeuf *et al.*¹⁴ studies the angular momentum of transition on NICS using CMO-NICS and suggests similar conclusions. We shall return to the consequences and support for this explanation later. Since the HOMO-LUMO gaps in $4n$ π electrons systems are smaller than the HOMO-LUMO gaps in $(4n+2)$ π electrons systems it is important to note here that (a) the paratropic currents in the former are generally stronger than the diatropic currents in the latter, since transitions between energy levels are proportional to ΔE^{-1} between the respective levels, and (b) it is important to include configuration interactions (CI) in the calculations of the induced ring currents (and the resulting induced magnetic fields), due to the energy proximity of the empty orbitals in $4n$ π electrons systems. Conversely, the calculations of the induced ring currents and induced magnetic field of $(4n+2)$ π electrons systems are much less sensitive to the inclusion of CI.

Phenomenologically, it is well established that aromatic compounds exhibit diatropic ring currents under external magnetic field and antiaromatic compounds exhibit paratropic ring currents under the same conditions. The question that is raised here (and will be answered later) is whether the appearance of diatropic and paratropic ring currents under external magnetic fields is limited only to aromatic and antiaromatic compounds. In other words, is the presence of an induced ring current under an external magnetic field a sufficient or only a necessary condition to define a system as aromatic (or antiaromatic)?

There are mainly four criteria for aromaticity: energy, structure, electron density based indices¹⁵ and magnetic properties. The first two have been discussed recently¹⁶ and in this issue of *Chemical Society Reviews*. The third, electron density based criteria, was reported by Solà and coworkers to be “the most accurate among those examined” in the comprehensive comparison they conducted in 2008.¹⁷ However, all three of these criteria are beyond the scope of this article. Magnetic criteria are currently the most popular methods and include NMR chemical shifts of ^1H , ^3He and Li^+ , magnetic susceptibility anisotropy, magnetic susceptibility exaltation, Nucleus Independent Chemical Shifts (NICS), Aromatic Ring Current Shielding (ARCS) and Current Density Analysis (CDA) plots. We will focus our attention on ^1H -NMR techniques and the two computational methods NICS and CDA, which are most in use today.

NMR chemical shifts. The ring current model (RCM)¹⁸ suggests that, for a $(4n+2)$ π electrons system, the diatropic ring current will form an induced magnetic field which is opposite to the external field at the center of the current. The lines of this magnetic field are curved (see Figure 1) and outside of the ring they are in same direction as the external field. Thus, protons that are outside of the ring experience a

downfield shift, while protons which are inside the ring experience an upfield shift. In $4n \pi$ electrons systems a paratropic ring current is induced, thus the effect on the external and internal protons is exactly the opposite. This model was challenged,¹⁹ but a response to this challenge advocated that the model is valid.^{20, 21} Thus, chemical shifts of protons can and have been used to identify aromatic and antiaromatic compounds. An extension of the use of NMR to assess aromaticity was developed mainly by R. Mitchell.²² This and the conclusions regarding NMR as an aromaticity-determining tool are discussed below.

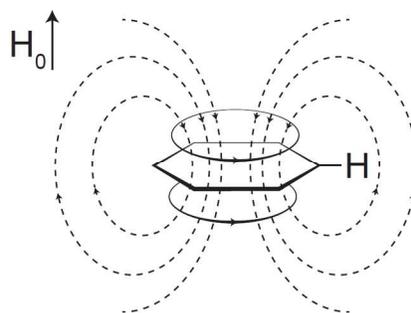


Figure 1. Ring current and induced magnetic field in benzene.

Magnetic susceptibility exaltation:²³ This method is based on the empirical observation that for non-aromatic systems the experimental magnetic susceptibility can be predicted from the magnetic susceptibilities of the atoms with some correction factors. Aromatic systems show a magnetic susceptibility that is larger than the one calculated from the atoms and this difference is termed exaltation. This method was popular during the 60s-80s of the last century. Nowadays, mainly due to the difficulty of quantifying aromaticity with this method and the need for an empirical reference, together with the development of computational methods that allow a more detailed and direct study of the magnetic properties, in a qualitative and quantitative fashion, this method is rarely used. Thus, a CAS search of the topic “Magnetic susceptibility exaltation” in the last ten years yielded 51 results. None of them is an experimental measurement of the property and most of them are used as computational evidence for aromaticity of the studied compounds, mainly in comparison to other criteria of aromaticity, such as the recent demonstration by Andjelkovic *et al.*²⁴ Since the experimental measurement of magnetic susceptibility exaltation is almost non-existent and computationally there are better methods for assessing aromaticity (see below), this topic will not be further discussed here.

It should be emphasized that neither aromaticity nor ring currents are measurable quantities. However, both NMR chemical shifts and diamagnetic susceptibility exaltation are experimentally measurable quantities that result from ring currents. The following two methods, current density analysis (CDA) and nucleus independent chemical shifts (NICS) are computational only.

Current Density Analysis (CDA). This method visualizes the ring current *via* arrows. The direction of the arrows (clockwise or anticlockwise) describes the type of the current (paratropic or diatropic) while the size of the arrows indicates the strength of the current. The most popular methods for current density analysis are the Continuous Transformation of Origin of Current Density – Diamagnetic Zero (CTOCD-DZ)²⁵⁻²⁷ also known as the ipsocentric method.^{11, 12, 28} Two other CDA methods are the anisotropy of

induced current density (ACID)²⁹ and gauge including magnetically induced current (GIMIC).³⁰ The main advantage of the CDA methods is the pictorial representation of the ring current/s in the system. For example, it is easy to see that, pentalene has a global paratropic ring current and two small local paratropic currents,^{31, 32} something that would be difficult (although not impossible, see below) to see with other methods. There are, however, some disadvantages to this method. Firstly, it is not easy to quantify. Thus, assuming that aromaticity is quantitatively related to the strength of the induced current (see below), most CDA methods cannot assess relative aromaticities of different systems, at least not in a straightforward way. Secondly, the pictures obtained with CDA cannot be decomposed to their components.³³ For example, the CDA of anthracene is consistent with a global anthracenic circuit, two “semi-global” naphthalenic circuits and three local benzenic circuits, but also with three local benzenic circuits (where the one at the central ring is stronger than the two in the terminal rings) only.³⁴ Thirdly, obtaining a CD map is not trivial. Most procedures are not embedded in popular commercial software,³⁵ thus, are used almost exclusively by professional computational chemists.

Nucleus Independent Chemical Shift (NICS). This is, by far, the most popular method for determining the magnetic properties of molecules.³⁶ It is implemented in most commercial software and is easy to calculate. NICS was invented in 1996 by Schleyer and coworkers,³⁷ who have since continued to do a lot of work with it.³⁸ So, what is NICS and how does it work? NICS uses a ghost atom (termed “bq” after the ghost Banquo in Shakespeare’s *Macbeth*), namely, one with no protons, neutrons or electrons, which is placed at any desired location. This ghost atom is nothing but a sensor for the magnetic environment at the point where it is placed, much like a thermocouple placed at a given point to measure temperature at this point. Actually, a thermocouple does not measure temperature directly, but changes its resistance or produces an electronic potential and has to be connected to an instrument that translates these changes into temperature. In analogy, the ghost atom senses the magnetic environment and reports the chemical shielding (absolute chemical shift) through the use of an adequate computational procedure, usually GIAO³⁹⁻⁴¹ and sometimes IGLO.^{42, 43, 44} The NICS value is taken as the negative of the calculated shielding, such that a negative NICS values indicates a diatropic magnetic field and a positive value a paratropic magnetic field. As a matter of fact, one does not need the ghost atom to calculate the magnetic environment at any desired location, and this forms the basis for the ARCS methodology,⁴⁵ but treating the probe as an atom is very appealing in all respects. The drawback of NICS is that it reports one numerical value at a given point, with no information regarding the source of the magnetic field that it senses. As a result, there have been many over-interpretations and some misinterpretations of NICS, some of which will be discussed below. Several NICS-based methods have been developed to overcome the aforementioned drawback, and they will be discussed in the appropriate chapter below. It should, however, be emphasized that nowadays NICS is the most popular method for the assessment of (anti)aromaticity of molecules.

Are magnetic properties sufficient to define a system as aromatic (or antiaromatic)?

Aromaticity is not well defined quantitatively or even qualitatively.¹⁶ Thus, the question that is posed in the title may be regarded as illogical. Nevertheless, an attempt to give an answer is presented here.

The term “aromatic” (or “aromaticity”) means different things in different fields of chemistry. For a biochemist, it will probably mostly mean a moiety that is involved in a special type of intermolecular interactions. For a synthetic organic chemist, it means stability under different reaction conditions (e.g., hydrogenation of olefins) although highly unsaturated, and a characteristic reactivity (e.g., electrophilic aromatic substitution). Physical and theoretical chemists usually look at the magnetic properties. Thus, until an accepted definition of aromaticity is presented to the community (by, for example, IUPAC), in many ways aromaticity is like beauty, namely, in the eyes of the beholder.

The magnetic properties of aromatic (and antiaromatic) compounds are the result of a cyclically conjugated π system. Typically, this conjugation is a result of properly aligned p orbitals, each containing one electron (e.g., the p orbital in an sp^2 -hybridized carbon atom), two electrons (for example, the lone pairs of nitrogen and oxygen atoms) or zero electrons (e.g., boron). However, conjugation may be achieved through “saturated” moieties if properly aligned. For example, the π orbital of CR_2 (Figure 2) can serve as a conjugating unit, allowing the generation of an induced ring current in, for example, cyclohexadienyl and cycloheptadienyl cations.⁴⁶ Perhaps the best example is cyclopentadiene and its 1,1-disubstituted derivatives. Indeed, it was claimed that the cyclopentadiene-based molecules⁴⁷ can become aromatic or antiaromatic, depending on the substituents at the 1 position.^{48, 49} The same type of ring currents were found in the ground and lowest excited states of pentafulvenes, which, orbitals-wise are closely related to cyclopentadienes.⁵⁰ This claim is based on the magnetic properties of the systems (NICS and ACID). However, despite the fact that cyclopentadiene derivatives exhibit an induced ring current under external magnetic field, organic chemists find it difficult to accept that these molecules are aromatic or antiaromatic, as their reactivity is different and they do not show a pronounced stability (see above). Indeed, it was concluded that these molecules are simply non-aromatic.⁵¹ Thus, there are molecules and ions that have characteristic magnetic properties of aromatic/antiaromatic molecules, yet they are not. The only possible conclusion, therefore, is that magnetic properties are necessary but not sufficient to define a system as aromatic (or antiaromatic).⁵²

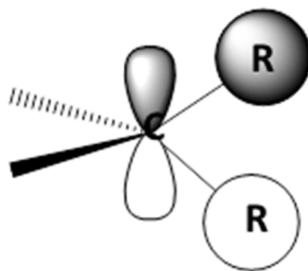


Figure 2. The π orbital of a saturated CR_2 fragment

The relationship between aromatic stabilization energy and magnetic properties.

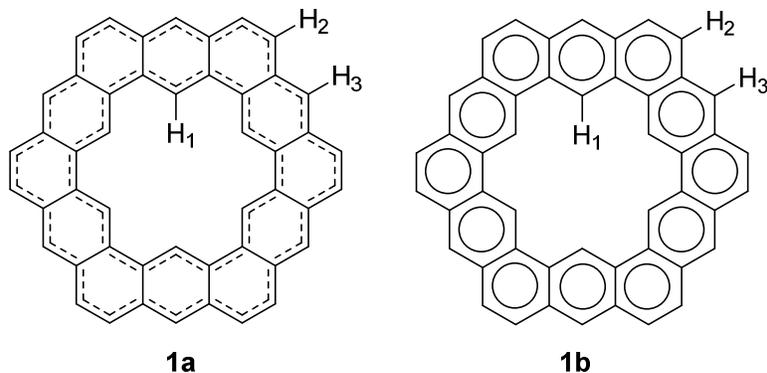
Some claim that aromaticity is a multidimensional phenomenon and therefore there is no connection between the different indices of aromaticity. Others object to this,⁵³ claiming that all molecular

properties are included in the molecular wave-function and are thus related. Indeed, there have been many attempts to correlate different aromaticity indices.⁵⁴ The geometry-based indices have been called into question,^{16,55} thus we deal here with energy and magnetic criteria.

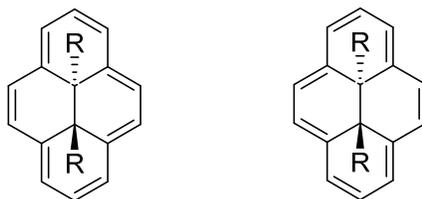
Although there are quite a few correlations between magnetic properties and aromatic stabilization energies (ASE),⁵⁶ there is an inherent problem in such correlations, and that is the definition of ASE. The ASE is defined as the stabilization energy relative to a non-aromatic reference system. There is, however, no good and general definition for this reference (this is shortly discussed in Reference 16). Other energy-based methods for estimating the stabilization by aromaticity, such as resonance energy (RE), resonance energy per electron (REPE), isodesmic reactions that compare proton affinity of the compound under study to that of an open-chain polyene analog, etc., suffer from similar problems. One way to circumvent this problem is to use relative energies within a series of compounds that differ from each other only by their aromaticities.⁵⁷ Another way is to find an energy measure that does not require reference systems.⁵⁸ It should be noted that recently Chauvin and Lepetit suggested a way to devise a general non-aromatic model for obtaining ASE,⁵⁹ however, this method has not manifested itself as yet in correlations that are discussed here. In summary, correlations between ASE and other aromaticity criteria (including magnetic) exist, but there is no general quantitative relationship between these aromaticity indices.

NMR

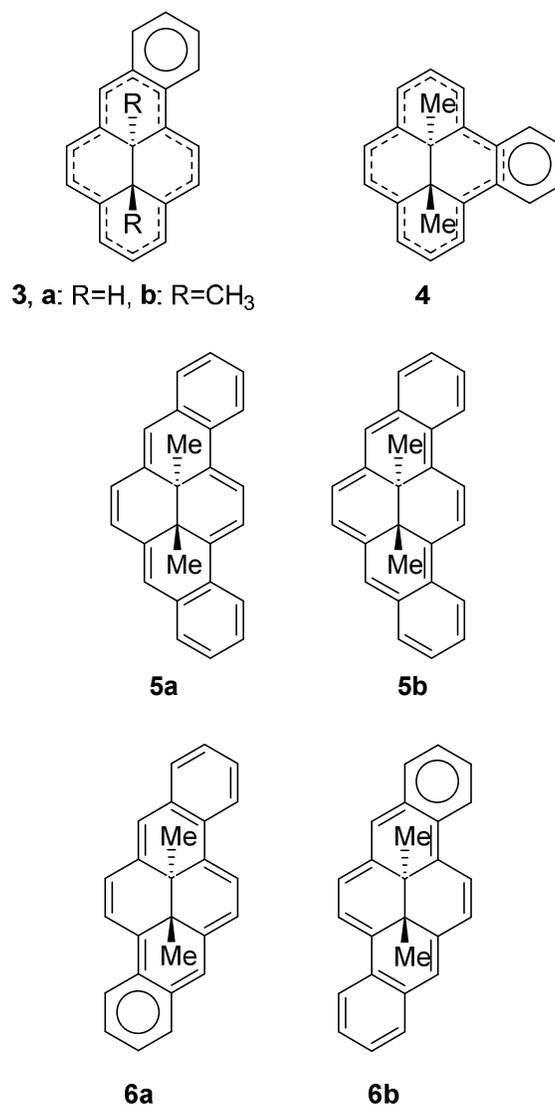
NMR is probably the most direct (experimental) way to observe the effects of the ring currents. As explained above, the RCM model suggests that, in aromatic systems, protons outside the cycle will experience a downfield shift while the protons inside the system will experience an upfield shift. Indeed, in larger annulenes this is exactly the picture. Another representative example is Kekulene – **1**. This molecule can be thought of as [18]-annulene within [30]-annulene (**1a**), or as a series of fused benzene rings (**1b**). H₁, which is inside the two annulene cycles, should exhibit an upfield shift in **1a** or a normal aromatic downfield shift for **1b**. The chemical shift of H₁ is 10.45-10.47 ppm, while those of H₂ and H₃ are 7.95-8.45 ppm (depending on the solvent), suggesting that **1b** is the correct way to describe the system.⁶⁰ NMR is thus the default experimental way to identify aromatic and antiaromatic moieties in molecules. However, due to the many effects (besides aromaticity) that influence the chemical shift, the ¹H NMR chemical shifts can be considered only as a qualitative measure of aromaticity. This topic has been reviewed,^{22, 61} and will not be discussed here. This chapter will focus on the quantitative measurements of aromaticity using NMR, work that was carried out mainly by R. Mitchell and his research group.



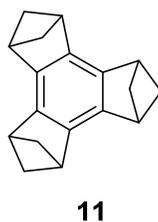
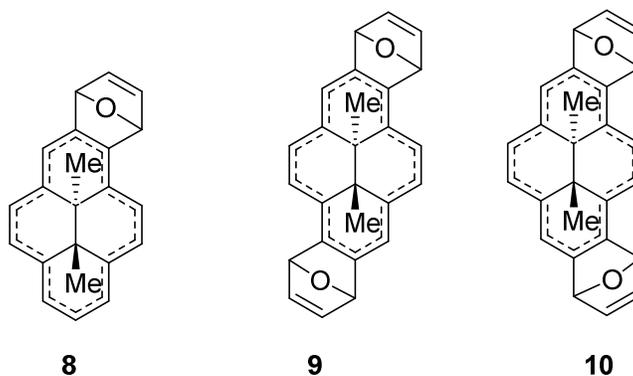
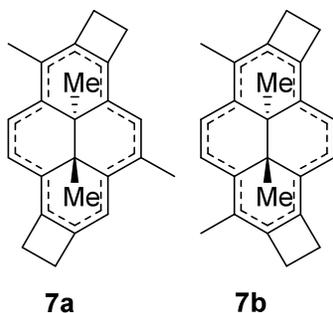
Mitchell has used **2** as an “aromaticity probe”.⁶² When unsubstituted, the two canonic forms, **2i** and **2ii**, have equal weight in the VB wavefunction, resulting in a 14e diatropic current, causing an upfield shift of the H (in **2a**) and Me (in **2b**) to -5.49 and -4.25 ppm, respectively. Any annulation that interferes with the equal weights of **2i** and **2ii** will decrease the ring current in **2** and therefore the chemical shifts of the H and Me in **2a** and **2b**, respectively, should have a smaller upfield shift. The explanation is given in the 1990 paper,⁶³ and principally rests on looking at the relative resonances of the annulene vs. the annulated moiety. In a series of papers,⁶⁴⁻⁶⁸ Mitchell showed that when a benzene is annulated (**3** and **4**), the chemical shift of the central H and Me are shifted downfield by 4.14 and 2.65 ppm, respectively, for **3**, and by 2.4 ppm for **4**. For **5** and **6**, it was found that the chemical shift of the central Me groups are 0.02 and -3.58 ppm, respectively. This can be explained on the basis of the canonic structures of **5** and **6**. Thus, in **5b** there is no double bond at the annulation position, destroying the aromaticity of the annulated rings. Therefore, **5a** will have much greater weight in the wave-function, overall reducing the ring current, as observed by the chemical shift of the Me. On the other hand, the resonance structures **6a** and **6b** each have a single bond at one annulation and a double bond at the other annulation, rendering them equal, thus regaining the 14e ring current as in the non-annulated system.



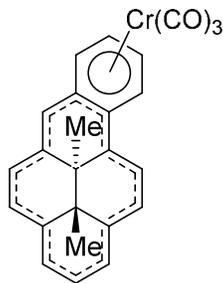
2i, a: R=H, b: R=CH₃ **2ii, a: R=H, b: R=CH₃**



Mitchell used this 14-annulene probe for the experimental study of several annulated moieties. For example, systems like **7**,⁶⁹ and **8-10**⁷⁰ were prepared in order to investigate the Mills-Nixon effect. It was found that annulating a four-membered ring does not reduce the ring current, therefore, and in accordance to computations,⁷¹ does not localize the system. On the other hand, a bicyclic annulation (**8 - 10**) reduces the ring current, in accordance with the bond localization that was found in the closely related **11**.⁷² Other moieties, such as cyclopentadienyl anion⁷³ and cycloheptatrienyl cation,⁷⁴ were also annulated to the annulene and found to be aromatic. During these studies, an empirical formula connecting the chemical shift of the central Me groups with the aromaticity of the annulated moiety was proposed.



By measuring the chemical shifts (and structural properties) of **12** and other transition metal complexes, Mitchell concluded that, e.g., the benzene moiety in $(\text{CO})_3\text{Cr}(\text{benzene})$ is more aromatic than benzene, as the chemical shift of the central Me groups in **12** is at lower field than that of **3** and **4**.^{63, 75-77} This contradicts chemical intuition for several reasons, two of which are mentioned here. One of the typical reactions of aromatic systems is electrophilic substitution. $(\text{CO})_3\text{Cr}(\text{benzene})$ undergoes nucleophilic substitution. The bonding of the metal to the benzene involves π electron donation from the benzene to the Cr and back-donation from the metal to the π^* orbitals. This causes bond alternation and elongation with C-C bond lengths of 1.405 and 1.424,^{78, 79} considerably longer than the C-C bond length in benzene.

**12**

In order to understand why the transition metal complexes that were studied with Mitchell's probe show these results, one has to re-examine the underlying assumptions, the main of which are: (a) reduction of the ring current in the 14-annulene is caused solely by localization of the system, namely, by unequal contributions of the resonance structures **2i** and **2ii**. (b) The aromaticity of the annulated moiety is the only factor that controls the relative contribution of the resonance structures **2i** and **2ii**. (c) The π systems of the 14-annulene and the annulated moieties are separated and can be handled as if these are two separated molecules. Now, let's examine these assumptions.

(A) Principally speaking, the reduction of the ring current may also be due to smaller electron densities. Thus, when an electron withdrawing moiety (π acceptor) is annulated to the 14-annulene, it may result in the total reduction of the electron density and non-symmetric distribution of the π electrons within the 14-annulene. Both will result in the reduction of the ring current. As metal carbonyls are electronegative, this may well be the reason for the observed results. (B) It has been shown that σ effects are responsible for geometrical localization of aromatic systems.^{71, 80, 81} The NICS-scan of $(\text{CO})_3\text{Cr}(\text{benzene})$ shows that the NICS_{ZZ} is similar to that of benzene, but the NICS_{XY} of the complex is far more diatropic than that of benzene, suggesting strong σ effects rather than π effects.⁸² (C) Many current density studies show that in most polycyclic systems there are global ring currents that spread out over the entire system. There is no particular reason why this should not be the case in the 14-annulene derivatives.

To the best of our knowledge, none of these possible reasons has been investigated so far and therefore there is no good answer to the question why transition metal complexes behave (in Mitchell's system) as if they are very aromatic.

In conclusion, a quote by Schaad⁸³ is brought here: 'L.J.S. remembers moderating a theoretical discussion of aromaticity ("Bar facilities will be available during this session") at the ISNA 5 meeting where at intermission he was surrounded by participants wanting to straighten out his ideas. While one on the right was saying "We must use NMR chemical shifts as the true measure of aromaticity", another on the left at the same time was saying with equal conviction "Whatever we do, we must not use NMR to define aromaticity"'. Despite the many years that have passed since ISNA 5, the situation has not changed, and it is probably still true that NMR quantitative aromaticity results must be handled with caution.

NICS

Since its inception in 1996,³⁷ the NICS methodology has consistently undergone modifications, refinements and improvements. In this section we will describe the various versions and methodologies of NICS. The first decade of NICS was previously reviewed and the reader is referred to that in-depth report.⁵⁶ This review will, therefore, emphasize the developments since 2005, and only briefly detail the modifications and revisions introduced during 1996-2005.

Nucleus Independent Chemical Shift is a tool that is ingenious in its simplicity (see the introduction). NICS can be used to assess the magnetic field at any desired location and its most common use is in the evaluation of aromaticity. Simply put, an aromatic (or antiaromatic) compound generates induced ring currents when placed into a magnetic field. These currents, in turn, create an induced magnetic field. The induced magnetic field affects the chemical shift of the nuclei in the compound. Thus, the chemical shift may be used as an indicator of the direction and magnitude of the induced magnetic field. This behavior was utilized previously, by using bridgehead atoms⁸⁴ or Li⁺ ions^{85, 86} as probes. However, since the nucleus of the probe itself affects the chemical shift calculated, the results are questionable. The significance of the NICS probe lies in the fact that it has no nucleus, and therefore acts as an innocent observer. The many different NICS and NICS-based methodologies to determine aromaticity all harness this indicative change in chemical shift. They differ mainly in the number and placement of the bq's and in how the calculated chemical shift is dissected into its components (or not). For the sake of clarity, the discussion will be divided into two parts: single-point NICS calculations and multi-dimensional NICS scans.

Single-point NICS

In their pioneering paper,³⁷ Schleyer and coworkers calculated the NICS values, defined as “the negative of the absolute magnetic shielding”, of a series of five-membered heterocyclic compounds (Figure 3) and found them to correlate well with ASE (aromatic stabilization energies), while not necessitating a reference non-aromatic standard or calibration *via* homodesmic/isodesmic equations. In addition, unlike magnetic exaltation, NICS was shown to be independent of ring size, though the authors demonstrated that it does depend on the number of π electrons. This first generation of NICS suffered from several practices and assumptions that would later become points of debate and a basis for improvement. Among these, the placement of the NICS probes at the geometric center of rings⁸⁷ was very problematic. The NICS values were reported with reversed signs, so as to agree with NMR chemical shift convention. Thus, negative and positive values were observed in aromatic and antiaromatic compounds, respectively. This practice was later criticized for causing over-interpretation of results.^{16, 88} Schleyer and coworkers noted the difficulty in using NICS for three-membered rings, due to the local shielding effects

of nearby σ bonds, yet stated that these effects were not significant in larger rings, a claim that would be corrected in later years.

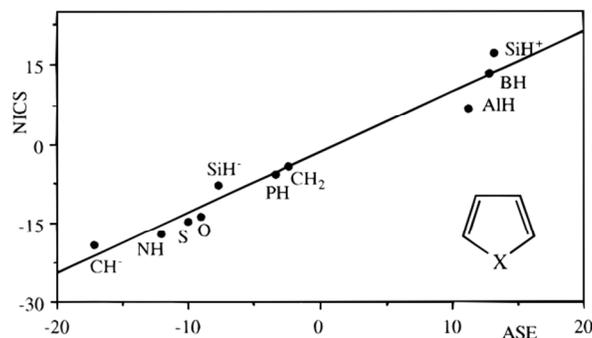


Figure 3. Plot of NICS(0) (ppm) vs the ASE (kcal/mol) for a set of five-membered ring heterocycles, C_4H_4X ($X =$ as shown). Reprinted with permission from Reference 37. Copyright © 1996 American Chemical Society.

A year following their initial publication,³⁷ the developers of NICS introduced two modifications.⁸⁹ Firstly, they raised the bq 1 Å above the molecular plane, hence termed NICS(1). In contrast to their original claim, it became apparent that NICS(0) contains a lot of σ contributions. Since σ contributions are short ranged, raising the bq significantly reduces the σ contaminations. NICS(1) was also chosen as a better aromaticity index based on a 2D grid study.⁹⁰ Secondly, they separated the total NICS value into σ and π contributions. Since aromaticity results from the π system of a compound, the authors attempted to calculate the clean π contribution to the NICS value. In this methodology, termed “dissected NICS”, and subsequently renamed LMO-NICS (localized molecular orbitals-NICS), the NICS(π) component was isolated using the IGLO⁴² (Individual Gauge for Localized Orbitals) computational method, which provides contributions from individual localized MOs to the NMR chemical shifts, and the Pipek-Mezey localization procedure. A correlation between NICS(π) and other indices of aromaticity (ASE and magnetic exaltation) was shown. However, this form of NICS suffers from several disadvantage: IGLO is gauge-dependent, thus less dependable than the gauge-independent GIAO⁴⁰ (Gauge Independent Atomic Orbital) procedure. Inherently, since a σ - π separation is performed, this method is useful only for planar systems. Non-planar compounds, or those with substituents that are non-planar, will have “contaminated” π orbitals. Finally, from the practical aspect, IGLO is not included in some of the more popular software packages while GIAO is.

A second version of dissected NICS, originally termed MO-NICS⁹¹ and later CMO-NICS (Canonical Molecular Orbitals-NICS), uses the canonical molecular orbitals that make up the shielding tensor to identify the contribution of the π orbitals and the GIAO⁴⁰ procedure. An alternate implementation of CMO-NICS was suggested by Bohmann *et al.*,⁹² using the natural chemical shielding procedure, which is included in the NBO 5.0g⁹³ and NBO 6⁹⁴ programs.

Following the initiation of dissected NICS methodologies, Steiner and Fowler^{95, 96} suggested that using the isotropic value of NICS was problematic, as the isotropic value disguises significant features of the different components. As aromaticity is a π -system property, and the π -system is perpendicular to the

molecular plane, a much more suitable indicator is the out-of-plane component of the shielding tensor. For planar compounds situated in the XY plane, this is the ZZ component, hence this value has been termed NICS_{ZZ} . However, it is important to note that NICS_{ZZ} is not free from σ contributions, even in planar systems.

Finally, the most refined index, $\text{NICS}_{\pi ZZ}$,⁹⁷ combines the two above-mentioned fundamental modifications to NICS: it considers *only* the π contribution (using LMO or CMO methods), and *only* the ZZ component of the chemical shift tensor. Several studies have compared the results obtained with the various NICS versions.^{56, 98} The more refined indices (namely, $\text{NICS}_{\pi ZZ}$ and $\text{NICS}(1)_{ZZ}$) generally prove to be more accurate, as they “distill” the contribution of the π electrons to the NICS value, which is the only relevant effect of aromaticity and antiaromaticity.

The many variations of single-point NICS methods have been used with varying degrees of success to investigate the aromatic character of a large range of systems, including five-membered ring heterocycles,³⁷ inorganic rings,⁸⁹ annulenes,^{56, 97} and all-metal clusters.⁵⁶ In addition, single-point NICS have been used to shed light on mechanistic pathways and transition states (see Reference 56 for further information). However, NICS values may also be misleading, as in some cases they contradict other indices of aromaticity. An example of this is the “anthracene problem”:³³ Schleyer and coworkers interpreted the increased diatropicity of the central ring of anthracene as increased aromaticity.⁹⁹ However, increased aromaticity should be accompanied by increased stability, and it is widely reported in the literature that the middle ring in anthracene is, in fact, the most reactive towards addition reactions. Bultinck supplied an alternative explanation:³³ the co-existence of six separate ring currents (three benzenic, two naphthalenic and one anthracenic). Since the middle ring takes part in the most circuits, it has larger current density surrounding it, and therefore, a stronger induced field at its center.

Multi-Dimensional NICS

In 2001, Klod and Kleinpeter¹⁰⁰ utilized a 3D grid of NICS probes and presented the iso-chemical-shielding surfaces (ICSS) (Figure 4). These colorful maps enable quantitative calculation of the anisotropy effects of functional groups and the ring current effect of aromatic and antiaromatic systems, with the goal of assigning chemical shifts of stereoisomers. This method was used later¹⁰¹ for providing the anisotropies of a large range of compounds. However, the authors did not expand their investigations into the assignment of aromaticity/antiaromaticity. Moreover, the NICS values calculated with this method are isotropic, which are not appropriate for aromaticity assignment.

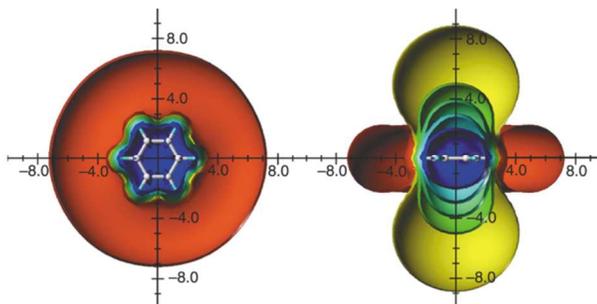


Figure 4. Calculated ring current effect of benzene (shielding surfaces at 0.1 ppm in yellow, at 0.5 ppm in green-blue, at 2 ppm in cyan and at 5 ppm in blue, respectively; deshielding surface at 0.1 ppm in red. View from perpendicular to the molecular (left) and in the plane of the molecule (right). Reproduced from Reference 100 with permission from The Royal Chemistry Society.

In 2006, the NICS-Scan method was introduced.¹⁰² At the same time, Solà and coworkers presented a similar methodology, applied to inorganic compounds.¹⁰³ The rationale behind the method used in both publications is that a single-point NICS measurement is not enough to characterize the aromatic behavior of a compound. However, since the physics of the induced magnetic field is known, a one-dimensional scan above the center of the system is enough to obtain the properties of the induced magnetic field. The obtained NICS values are then separated into the *in-plane* and *out-of-plane* components and plotted against the distance from the molecular plane. The shapes of the curves provide a much more comprehensive picture of the nature of the system than a single NICS value. Characteristic shapes can be interpreted as diatropic or paratropic ring currents and the results for several neutral, charged and triplet systems were shown to be much more consistent with other indices of aromaticity (Figure 5). It was also demonstrated that the diamagnetic and paramagnetic contributions to the *in-plane* component are similar for $4n \pi$ and $(4n+2) \pi$ systems. The diamagnetic contribution to the *out-of-plane* component is also similar for the two types of systems. The difference was found in the paramagnetic contribution to the *out-of-plane* component; while in aromatic compounds this contribution is smaller than the diamagnetic one and rapidly decreases with distance, in antiaromatic compounds this paramagnetic contribution is larger and decreases much more slowly with distance. Typical shapes for diatropic and paratropic systems are shown in Figure 5. While the NICS-Scan provides a dependable qualitative analysis of the magnetic behavior of studied systems, the values cannot be used for quantitative comparison, as was further demonstrated in another work.⁵¹

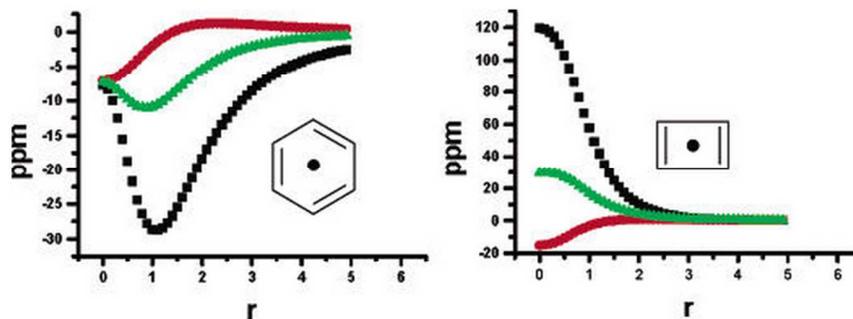


Figure 5. In-plane (red), out-of-plane (black) and isotropic (green) NICS values for benzene (left) and cyclobutadiene (right) as a function of distance. Reprinted with permission from Reference 102. Copyright © 2006 American Chemical Society.

In 2010, the σ -Only Model¹⁰⁴ was introduced. This is a chemical model designed to enable quantitative analysis with the NICS-Scan by mimicking the contribution of the σ electrons to the NICS values. Similarly to LMO and CMO, this model also aims at segregating the π effects from the σ effects of a given compound but, differently from these two methods, it is not grounded on a mathematical treatment of the orbitals, but on a chemical model, based on using the π electrons to bind Hs. The NICS values of the σ -only model are subtracted from those of the delocalized system, to give the clean π contribution, which correlates well to CDA results (Figure 6).^{57, 104} The method allows for quantitative comparison between ring currents of different systems, treatment of non-planar systems, and contains a built-in measure of goodness.

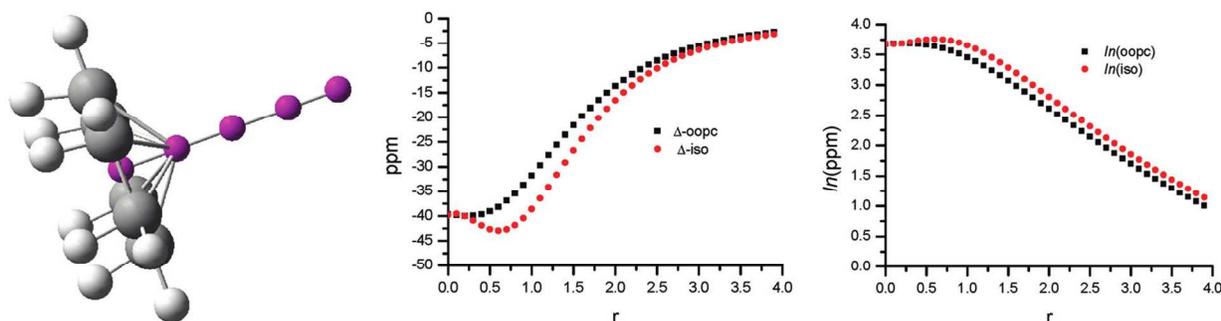


Figure 6. Three-dimensional structure of benzene with the Hydrogens of the σ -Only Model and the bq 's for the NICS-Scan calculation (left). Plots of Δ (out-of-plane) and 3Δ (isotropic) for benzene obtained with the σ -Only Model (middle). Natural logarithms of the plots for Δ (out-of-plane) and 3Δ (isotropic) (right). Reprinted with permission from Reference 104. Copyright © 2010 American Chemical Society.

The improvements to NICS methods enable a more accurate determination of the dia- and paratropicity of the π electrons, but have not dealt with the inability of NICS to determine the source of the induced ring currents and magnetic fields. This inability becomes crucial in polycyclic systems, where current density studies show that, in most cases, the currents are spread out over the whole system rather than

being localized within each ring (see below). In order to be able to use NICS and HOMA (both suitable for single-ring systems) the term “local aromaticity” was invented.¹⁰⁵ As aromaticity is a molecular property, local aromaticity, namely, the NICS value of one ring in a polycyclic system, is practically worthless for understanding the system, as shown for anthracene (see above). Also, other indices of aromaticity (e.g., ASE, RE) are molecular properties. Indeed, many years later the inventor of the term admitted that aromaticity is a molecular property.¹⁰⁶

Recently, in 2014, the NICS-XY-Scan¹⁰⁷ method was introduced. This methodology enables identification of local and global ring currents in polycyclic systems, using the NICS tool. This method is based on one (or more, if needed) 1-D scan(s) of NICS along a trajectory that crosses the axis (or axes) of the compound at a constant height above the system. The results of such scans show a much more comprehensive picture of the behavior of the induced magnetic field of the compound (Figure 7). The NICS-XY-Scan is quantitative when using NICS _{π zz} values (from either NBO-based CMO-NICS or the σ -Only Model), but it was also shown that the method could be used qualitatively for NICS_{zz} values at a height of 1.7 Å above the molecular plane. The results of the NICS-XY-scan method agree with CDA results, when these are available, and in some cases provide additional information. Thus, in the case of anthracene, the quantitative analysis supports Bultinck’s suggested interpretation³³ – a conclusion that had until then been ambiguous.¹⁰⁸

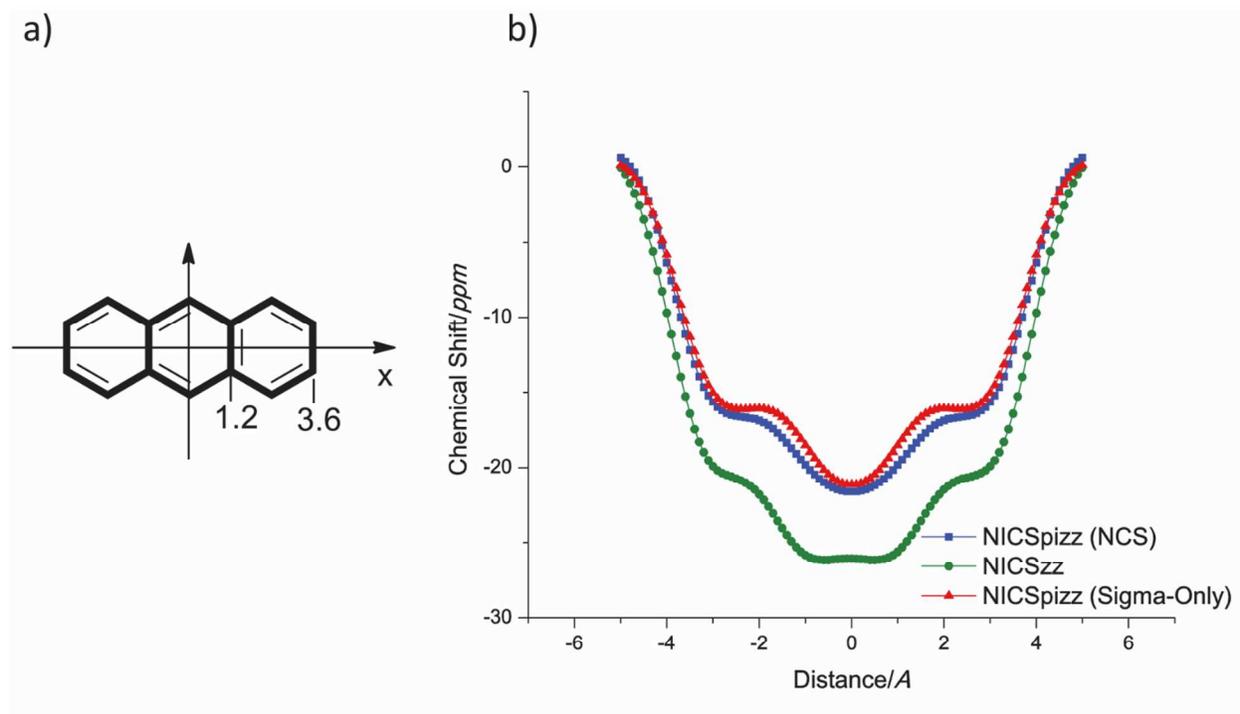


Figure 7. NICS-X-Scan of anthracene. a) Scheme of axis. b) plots of NICS _{π zz} obtained from NBO-CMO-NICS (blue), NICS_{zz} (green) and NICS _{π zz} obtained from the σ -Only Model (red) at a height of 1.7 Å above the molecular plane. Reproduced with permission from Reference 107. Copyright © 2014 John Wiley and Sons.

Selected Applications

Despite criticism that NICS is a “virtual” index,¹⁰⁹ due to an inability to corroborate results via experimental work, NICS remains an extremely popular tool. This is demonstrated by the hundreds of examples that may be found in the literature for its use in assigning aromaticity/antiaromaticity to various types of systems. We will highlight only a few case studies from recent years.

Solà and coworkers have thoroughly compared many different indices of aromaticity in a variety of contexts, in an effort to determine the limitations of the various methods. They used NICS, ASE, geometry-based methods, and an electron delocalization index to obtain a better understanding of the substituent effect,¹¹⁰ the effect of bending,¹¹¹ and the effect of distortion¹¹² on the aromaticity of benzene and benzenoids. Their results demonstrated the problems in using isotropic NICS values (NICS(0) and NICS(1)) were shown to give misleading results, while NICS(1)_{zz} gave more satisfactory results, and emphasized cases in which even refined NICS methodologies failed to give accurate answers.¹⁷ Based on these and other works,¹⁰³ the authors cautioned against using only one method to determine aromaticity and also warned against the use of single-point NICS, in general. Solà and coworkers also investigated the use of NICS in polycyclic compounds and determined that the NICS value of each ring is affected not only by the local current in that ring, but also by other, larger circuits including that ring and other unconnected circuits within the molecule.^{111, 113}

The Mills group has dedicated many years to the investigation of antiaromaticity, with a main focus on fluorenyl- and fluorenylidene-containing compounds (Figure 8). Using a combination of experimental and computational tools, they have studied the antiaromaticity of these compounds and have found correlations between NICS values and other indices, such as ASE,¹¹⁴ HOMA,¹¹⁵ redox potentials,¹¹⁶ and calculated and measured ¹H and ¹³C chemical shifts.^{117, 118}

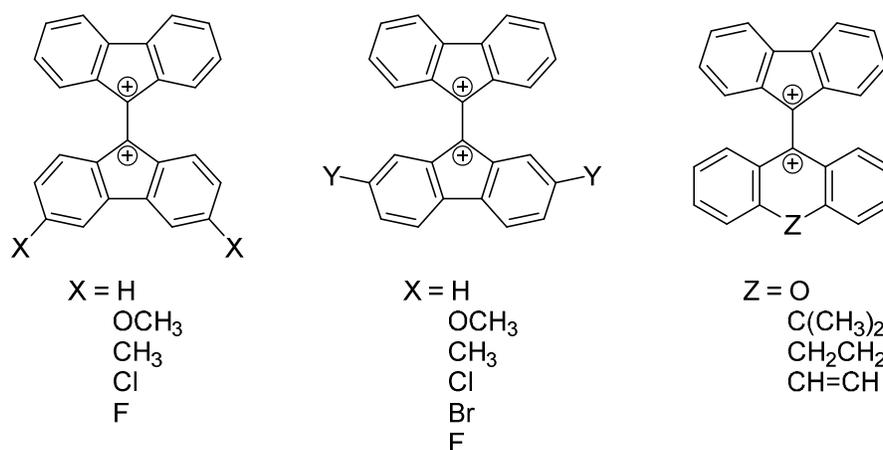


Figure 8. Some examples of the compounds studied by the Mills group.

In addition, Llagostera and Mills¹¹⁹ studied a wide range of neutral, anionic and cationic systems of varying aromatic, non-aromatic and antiaromatic character, and found that the different species exhibited respective correlations between $\Sigma NICS(1)_{zz}$ to magnetic susceptibility exaltation (Λ). Interestingly, when they compared $\Sigma NICS(1)_{zz}/area^2$ and $\Lambda/area^2$, all of the studied compounds could be

included in a general correlation, indicating that both indices are dependent on ring area. While this appears to stand in contradiction to previous results, according to which NICS is independent of size, one must note the different circumstances. When NICS is used to study monocyclic compounds, the values can be compared as is. However, when polycyclic species are studied and a sum of NICS values from the ring centers is calculated (such as in the case of Mills and Lagostera), the values must be calibrated, otherwise systems with more rings will – obviously – have larger NICS values. Thus, dividing the NICS value by area^2 serves as a calibration tool to allow comparison between systems of varying numbers of rings.¹²⁰

In 2006, Sebastiani¹²¹ proposed a method, similar to that of Klod and Kleinpeter¹⁰⁰ mentioned above, for calculating NICS in condensed-phase systems, using a pseudopotential plane-wave approach and obtaining the NICS map via an inverse Fourier transformation of the induced magnetic field, represented in reciprocal space. Sebastiani utilized this methodology to generate NICS maps for a calixhydroquinone-based nanotube and graphite (Figure 9), as well as nano-rings. It should be noted, however, that this method calculates the isotropic value of NICS, which is problematic in describing aromaticity, as detailed above.

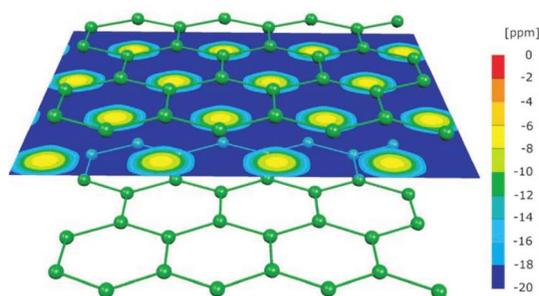


Figure 9. Section of the NICS field of graphite in the plane parallel to the sheets, taken $1 a_0$ below the atoms. Reproduced with permission from Reference 121. Copyright © 2005 John Wiley and Sons.

Recently, Radenkovic *et al.*¹²² studied the effect of benzo-annulation on the aromaticity of heterocyclic conjugated systems and also found that, for several systems, the NICS criterion does not agree with the geometric criterion (HOMA), multicenter delocalization index, and the pairwise energy effect.¹²³

NICS is not limited to organic compounds. It has been used to assign aromaticity to inorganic clusters and cages, as well. A great deal of work has been done by the Boldyrev^{124, 125} and Tsipis research groups.^{126, 127} Other examples include the work of Xu¹²⁸ *et al.* on Si_2BX ($X=\text{Li}, \text{K}, \text{O}, \text{S}$) clusters, the work of Liu¹²⁹ *et al.* on X_3^+ ($X=\text{H}, \text{Li}, \text{Na}, \text{K}, \text{Cu}$), and the work of Chakraborty¹³⁰ *et al.* on Na_2Mg_3 . However, most of these latter studies used isotropic NICS values, which are problematic. Recently, Baranac-Stojanovic used $\text{NICS}(0)_{\text{nzz}}$ and extra-cyclic resonance energies to investigate the aromatic behavior of 1,2-, 1,3-, and 1,4-azaborines. The order of aromaticity found in this work agrees with previous, geometry-based assignments. Yet, interestingly, the author concluded that the most aromatic isomer is also the least stable one, and suggested that the current prevailing notion that aromaticity and stability go hand in hand may be incorrect.¹³¹ However, assigning aromaticity to non-organic compounds and clusters has

also received some criticism, as “aromaticity” is a concept born of the organic world, and the question has been raised whether it can legitimately be extended to the realm of the inorganic.¹⁰⁹

Current Density

According to the ring current model (RCM), aromatic compounds support a diatropic current and antiaromatic systems support a paratropic ring current under external magnetic field.¹³² Thus, the aromaticity of a planar compound may be evaluated directly, either by calculating the intensity of the current or by calculating the current density in a given molecule when it is subjected to an external magnetic field, which is perpendicular to the molecular plane.

Two reviews published at the beginning of this century^{23, 109} extensively and thoroughly describe the historic methods of calculating the intensity of the ring current and the current density field. Lazzaretti¹⁰⁹ also details the mathematical and physical background of such methods. Thus, we shall refrain from repeating here the history and the mathematical developments of the field but focus only on the various *ab initio* methods developed to describe (and visualize) the current density field induced in a molecule under an external magnetic field, and how they have been used as a criterion of aromaticity.

Originally, many chemists, including Pople, Coulson, and McWeeny, devoted a great deal of effort to developing methods of calculating the intensity of the ring current.²³ With the advent of better computational capabilities, however, new methodologies that enable a pictorial representation of the current density field induced in a molecule were developed. These maps are a useful tool for identifying and comprehending features of aromatic compounds. An early version of current density analysis (CDA) was based on the techniques and concepts of differential topology^{133, 134} and was used to generate two-dimensional plots – *stagnation graphs* – of the three-dimensional current density vector field. Though this topological methodology allowed chemists to obtain a “feel” for the behavior of the induced current in space, it was not without its drawbacks. The plots were not easily interpreted, and, moreover, suffered from artifacts that could not be distinguished from actual physical features, due to the approximate nature of the calculations. In addition, second order magnetic properties, such as magnetizability, polarizability, and nuclear shielding, which are obtained by integration of the first order current density, were not accurately calculated by the original methods, due to the problem of gauge-dependence. Thus, the development of improved *ab initio* methods that address the issue of the origin of the vector potential (gauge) had a significant impact on the field of current density analysis methods.

Conventional approaches use a simple gauge origin [also known as a common origin (CO)], which is usually placed at the center of mass, and suffer from large paramagnetic and diamagnetic contributions that contaminate the calculation. The multiple-origin techniques IGLO⁴² (individual gauges for localized orbitals) and LORG^{135, 136} (Localized Orbitals/Localized Origin) are based on assigning different origins for different orbitals in Fock space. The IGAIM¹³⁷ (Individual Gauge for Atoms in Molecules) technique proposes the same rationale, with the exception that the multiple origins are in real space. The assumption is that more accurate estimates of the current density will be obtained if the origin of the coordinate system lies close to the point where current density is being evaluated. Indeed, in these

procedures, much of the spurious diamagnetic and paramagnetic contributions are removed, and these methods are much less dependent on the size of the basis set.

In 1993, a major advancement was made with the Ansatz of Keith and Bader, who recognized that the gauge origin need not be the same for all positions, but may be described by a single-valued function of the position that may be defined such that each grid point is chosen to be its own origin of the vector field. The authors formulated the numerical method CSGT¹³⁸ (Continuous Set of Gauge Transformations), to achieve this end, and enabled the calculation of high-quality approximations of the current density with much smaller basis sets than needed for CO methods. Lazzarotti commented¹⁰⁹ that the name CSGT does not accurately reflect the computational procedure taking place, and also pointed out that Keith and Bader's numerical approach could be replaced by a fully analytical solution, which he formulated and termed CTOCD¹³⁹ – Continuous Transformation of the Origin of the Current Density. Since the n -electron diamagnetic current density term at each grid point is formally annihilated by choosing that point to be its own origin of vector potential, he proposed the acronym CTOCD-DZ (Continuous Transformation of the Origin of the Current Density-Diamagnetic set to Zero).¹⁴⁰ Fowler and coworkers later renamed the method *ipsocentric*¹¹ to reflect the fact that in the CTOCD-DZ approach each calculated point is its own origin for that specific calculation.

Since the origin's shift function is based solely on the grid, and not on the wave-function, the ipsocentric approach enables unambiguous definition of the orbital partition of the total current density,¹¹ independently of the basis set used. In the context of aromaticity, this is a meaningful advantage, as it is possible to separate the current density stemming from the σ and π orbitals, respectively. In orbital terms, the total current is represented as a sum over virtual transitions from occupied orbitals to unoccupied orbitals of the cycle. The ipsocentric method excludes the contribution of any occupied-to-occupied virtual transitions, therefore yielding a physically non-redundant representation of the magnetic response. As a result, angular-momentum symmetry selection rules may be defined that classify orbital contributions as active or inactive, diatropic or paratropic. The current is paratropic when the transition is between orbitals with an equal number of angular nodes, and diatropic when the transition increases this number by one. Applying these rules has great significance for the physical interpretation of the induced current, and allows for easy rationalization of the relationship between the molecular electronic structure and the magnetic response.¹⁴¹ For example, based on these rules, Steiner and Fowler, strong proponents of the ipsocentric approach, demonstrated that a diatropic ring current in a $(4n+2)$ π aromatic cycle may be attributed almost entirely to the response of the four most energetic electrons, while for a $4n$ π antiaromatic molecule, the characteristic paratropic current is attributed mainly to the two most energetic electrons.¹² They also used spectral decomposition to further break down orbital contributions into explicit contributions from virtual excitations. Thus, they showed that the ring currents of benzene and planar-cyclooctatetraene (planar-COT) are dominated by the contributions of HOMO-LUMO virtual excitations, while the magnetic response of borazine can only be described with excitations beyond its valence space.¹⁴²

Another method developed, using a similar rationale, is the CTOCD-PZ.²⁷ According to this approach, it is now the paramagnetic component which is made to formally disappear. However, since any paramagnetic component of the current parallel to the induced magnetic field is orthogonal to the

diamagnetic current, no gauge transformation can annihilate this component. Therefore, instead, in the CTOCD-PZ method, only the perpendicular components of the paramagnetic current are annihilated.¹⁴³ This is achieved by shifting the origin to a point other than the grid point being calculated, hence Lazzarotti termed the method *allocentric*. This method is superior to the DZ method for calculation of magnetizability and shieldings, as convergence towards the Hartree-Fock limit is systematically improved, but the shift function is dependent upon the inverse of the electron density, thus it may have discontinuities when the density is zero. However, when appropriate numerical safeguards are used, the CTOCD-PZ method may be used safely for the computation of the total current density and evaluation of integrated magnetic properties.¹⁴⁴

Both of these methods, CTOCD-DZ and CTOCD-PZ, have been further modified. It was found that when they are used to calculate integrated properties, they both lead to poor heavy-atom shieldings. To correct this, an exponential “pushing function” was defined, which shifts the origin toward the nucleus. These refined methods, assigned the terms CTOCD-DZ2¹⁴⁵ and CTOCD-PZ2,²⁷ respectively, have both been tested and show significantly improved numerical results of integrated properties.

Soncini and Fowler¹⁴¹ computed maps for five representative compounds – benzene, cyclooctatetraene, borazine, tris(cyclobutano)benzene and tris(cyclobutadieno)benzene – and showed that all four methods (DZ, PZ, DZ2 and PZ2) give comparable results in the π plotting plane when implemented at the coupled Hartree-Fock (CHF) level, but vary in the calculation of nuclear shieldings. Hence, the authors recommended combining two methods in order to obtain maximum information: the resource-efficient DZ to give accurate and clear current maps, and the PZ2 to obtain numerical accuracy of nuclear shieldings. A few years later, Havenith and Fowler¹⁴⁶ also implemented the ipsocentric method at the DFT level, and showed that the results are essentially the same (Figure 10). Soncini *et al.*¹⁴⁷ also compared DFT results to HF and found that they are consistent for aromatic benzene and biradical *o*-benzene, but have some qualitative differences for planar-COT, highlighting the fact that correlation is important when paratropicity dominates.

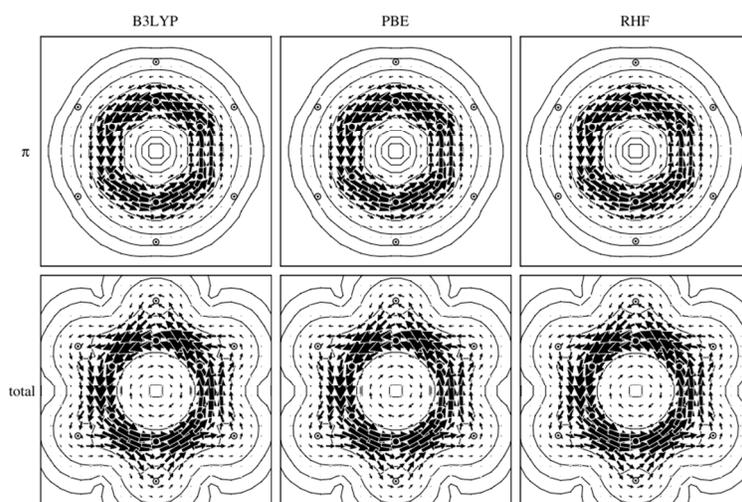


Figure 10. Plots of the π (top) and total (bottom) induced current density at a height of 1 Å from the plane of the nuclei for benzene, evaluated at B3LYP (left), PBE (middle) and RHF (right).¹⁴⁸

In 2007, Soncini extended the existing CTOCD-DZ computational approach to include open-shell systems,¹⁴⁹ creating the opportunity to investigate Baird's rules for open-shell systems. Baird predicted¹⁵⁰ that Hückel's $(4n+2)/4n$ law for the lowest closed-shell singlet states undergoes inversion, to the effect that the first triplet $\pi\pi^*$ -state $[4n]$ annulenes are aromatic.^{102, 151, 152} Indeed, using current density calculations for open-shell systems, Soncini and Fowler¹⁵³ re-validated Baird's prediction for triplet-state annulenes and quintet excited-state azulene.

Fowler proposed in 2002 the "pseudo- π " technique,¹⁵⁴ in which the framework of conjugated carbons is replaced by hydrogen atoms bearing single 1s (STO-3G) orbitals. The results of this resource-efficient approximation seem to reproduce the full calculation (Figure 11).

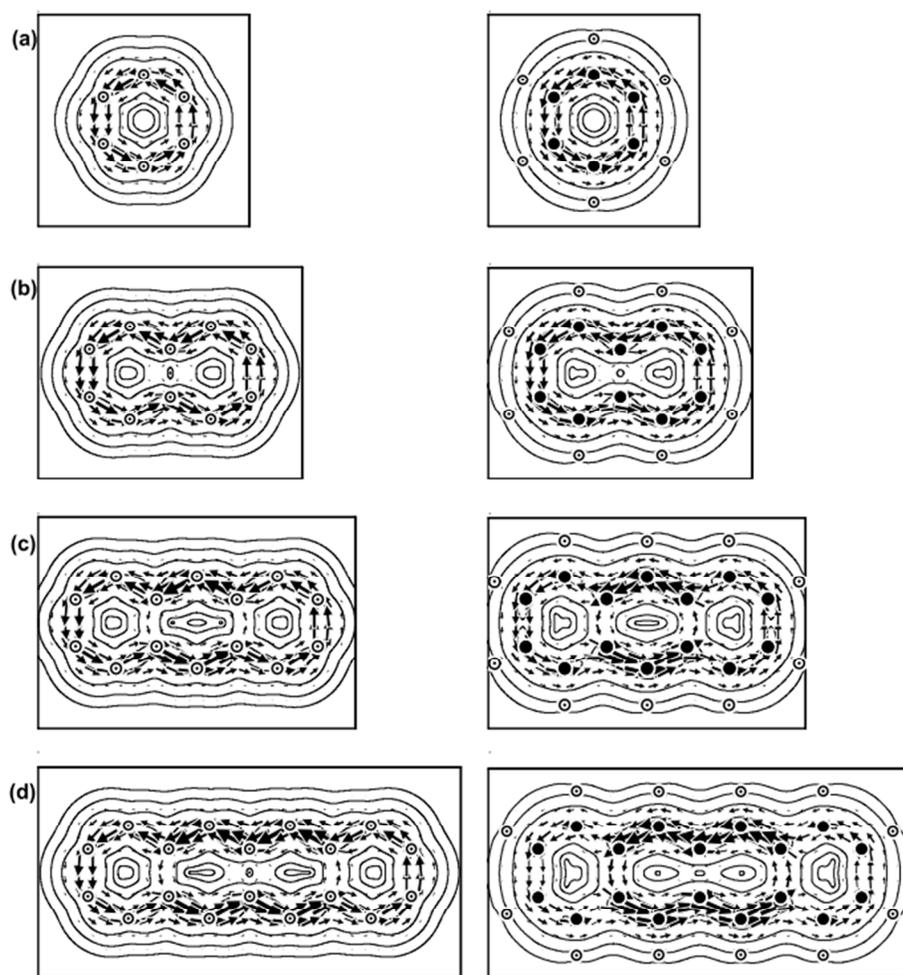


Figure 11. Comparison of in-plane pseudo- π (left) and (right) full ab initio computed π current densities for linear polyacenes a) benzene, b) naphthalene, c) anthracene and d) tetracene.¹⁵⁵

In 1998, Diederich and coworkers,¹⁵⁶ investigated aromatic transition states in non-planar compounds by plotting the anisotropy of the induced current density. Adopting this rationale, Herges and Geuenich^{29, 157} proposed in 2001 a general method for the visualization of delocalization and

conjugation, ACID (Anisotropy of Current-Induced Density). The authors noted that the method is derived from a quantum theoretical quantity, thus no parametrization is required, and results cannot be manipulated to fit existing data; and unlike current density analysis methods, it generates a scalar field, which is independent of the orientation of the molecule in the external magnetic field, and can be mapped as an isosurface (Figure 12 displays the ACID of benzene). ACID has been used to study the aromatic behavior of several molecules, and in the cases of naphthalene and coronene has indicated ring currents in the [10]- and [18]annulene periphery, respectively (Figure 13).

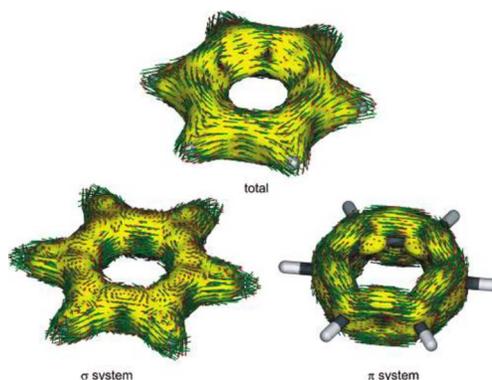


Figure 12. ACID isosurfaces of benzene separated into the σ and π contributions. Current density vectors are plotted on the ACID isosurface to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic). Reprinted with permission from Reference 29. Copyright © 2005 American Chemical Society.

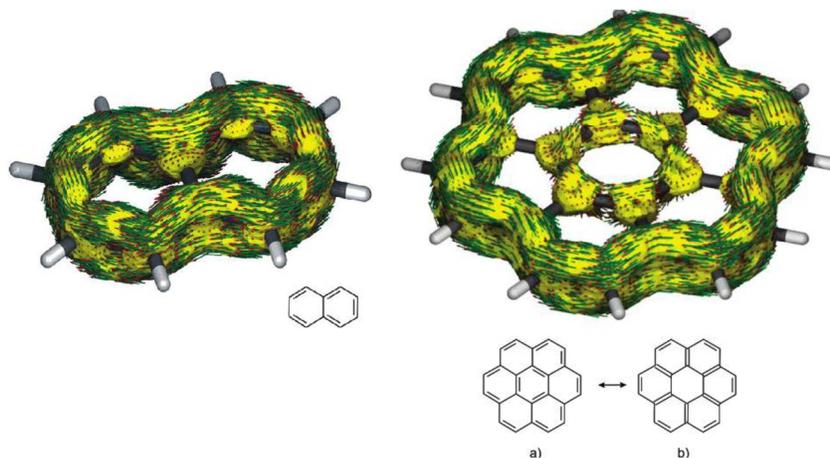


Figure 13. ACID of the π system of naphthalene (left) and coronene (right). The current density vectors plotted onto the ACID isosurface indicate a strong diatropic ring current in the [10]annulene periphery of naphthalene and the [18]annulene periphery of coronene. Adapted with permission from Reference 29. Copyright © 2005 American Chemical Society.

A second approach to eliminating the dependence on the gauge origin is based on GIAO.⁴⁰ Gauge-independent orbitals, also known as London orbitals, are invariant to change in the coordinate system. In 2004, Jusélius *et al.* published a new computational method that uses GIAO to calculate the various components of the magnetically induced current density tensor. Their method, GIMIC¹⁵⁸ (Gauge

Independent Magnetically Induced Current), is formulated within the framework of analytical derivative theory, hence it allows implementation at the HF-SCF and electron-correlated levels [DFT, MP2, CCSD, CCSD(T)]. A unique feature of this approach is that it extracts quantitative values for the induced currents, by numerically integrating the current flow. For example, the authors found the induced ring current of benzene (Figure 14) to be 11.4 nA T^{-1} at the CCSD(T)/TZP level.

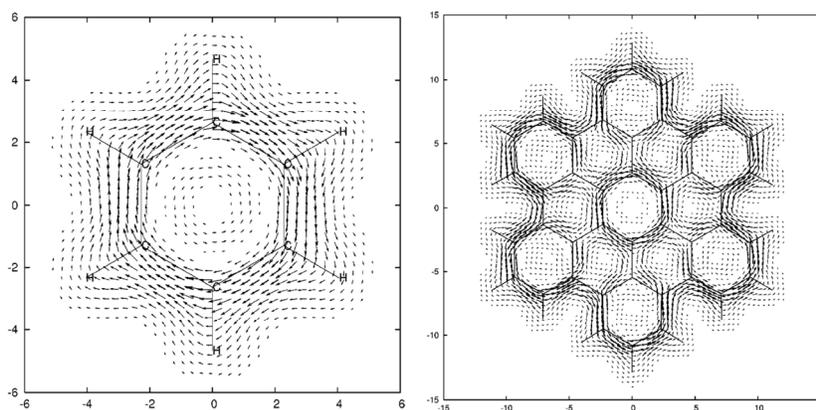


Figure 14. The induced current densities in benzene calculated at the HF-SCF/TZP (left) and hexabenzocoronene calculated at the DFT-BP86/TZP level (right). Induced currents are calculated at $1 a_0$ above the molecular plane using GIMIC. Adapted with permission from Reference 158. Copyright © 2004, AIP Publishing LLC.

GIMIC has been used to study the aromaticity of various types of compounds, including polyaromatic hydrocarbons (PAHs),¹⁵⁹ porphyrinoids¹⁶⁰ and Möbius-twisted molecules.¹⁶¹ Sundholm and coworkers have also applied GIMIC to inorganic compounds, such as Al_4^{-2} and Al_4^{-4} species¹⁶² and Mo and Cr oxides.¹⁶³ However, as stated above, the inclusion of non-organic species in the classification of aromaticity is a point of debate.

Selected applications

One of the main advantages of current density based analysis methods is the visual output, which makes it easier to intuitively comprehend the behavior of the ring current within the molecule. CD maps have been used to obtain an understanding of the ring currents in many simple and complex compounds. Examples can be found ranging from benzene and pyridine to porphyrins,^{164, 165} circulenes,¹⁶⁶ and Clar structures.¹⁶⁷ They have an especially important role in the analysis of polycyclic compounds, where conventional NICS methods have been shown to give misleading results (see above).^{33, 111, 168}

Maps have been computed for many interesting systems, and conclusions drawn from them often correlate well to other indices of aromaticity. Bultinck and coworkers studied several PAHs, including coronene, pyrene and triangulene, and the authors found correlations between current density maps and delocalization indices (Figure 15).⁵³

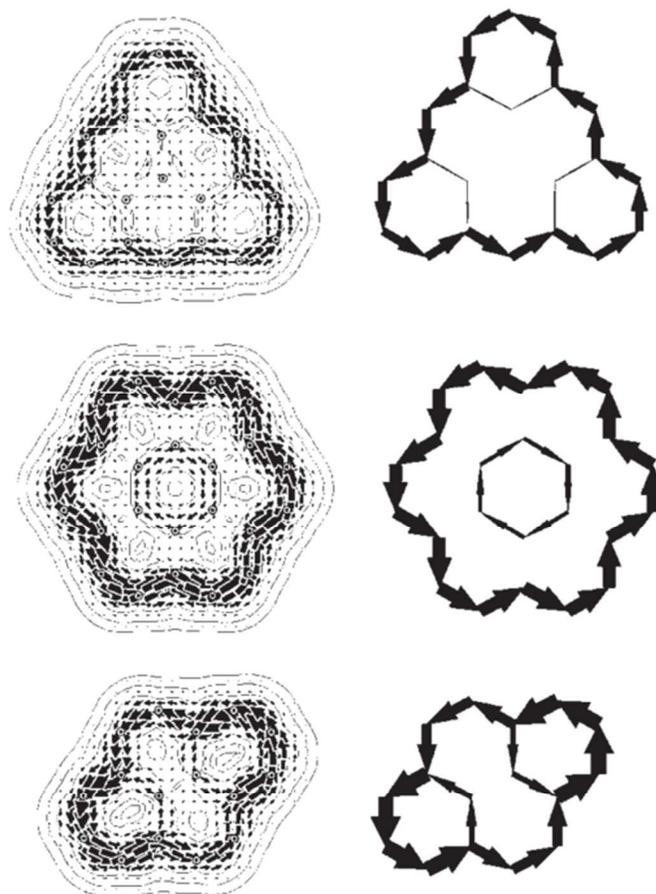


Figure 15. Ring current maps (left) and multicenter bond indices ring current maps (right) for triangulene (top), coronene (middle), and pyrene (bottom). Adapted with permission from Reference 53. Copyright © 2008 John Wiley and Sons.

Another interesting example of this is the phenalenyl motif, which Cyranski *et al.* termed “a magnetic chameleon”.¹⁶⁹ For this alternant compound, both the cation ($4n$ π electrons) and the anion [$(4n+2)$ π electrons] exhibit a diatropic ring current, which is counterintuitive to the universally accepted Hückel π -electron counting practice. Even more interestingly, when the central carbon of the 12π -electron cation is replaced with the isoelectronic boron, the direction of the induced ring current changes to paratropic, despite retention of the number of electrons. In other words, the direction (sense) of the current is dependent upon the central atom, but is independent of the total number of π electrons. These observations cannot be explained by other indices of aromaticity (ASE, NICS, HOMA, and magnetic exaltation), but the orbital decomposition within the ipsocentric approach reveals the different virtual excitations allowed by symmetry that give rise to the different patterns of current (Figure 16).

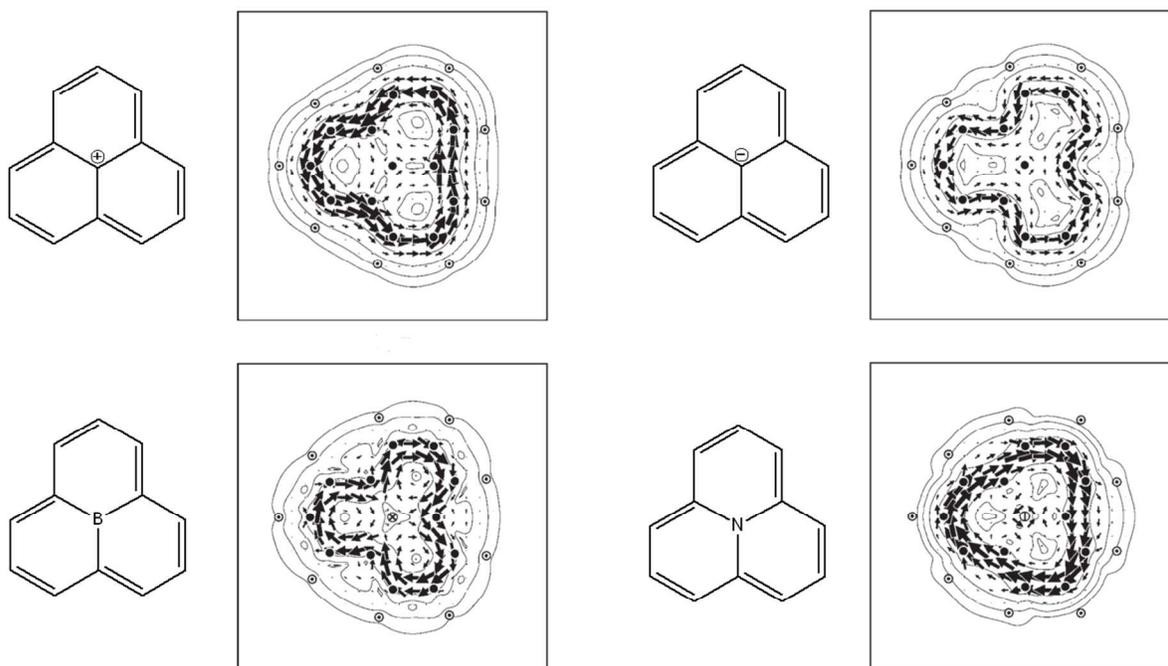


Figure 16. Structures of and current density maps for the compounds studied in Ref. 169. Maps are plotted in the plane $1 a_0$ above the nuclei. Vectors indicate the direction and intensity of the in-plane current and contour/shading the total magnitude. Anticlockwise (clockwise) circulations represent diatropic (paratropic) ring currents. Adapted with permission from Reference 169. Copyright © 2007 John Wiley and Sons.

GIMIC has also been gaining popularity in recent years. Kaipio *et al.*¹⁵⁹ studied the effect of Fluorine substitution on the aromaticity of polyaromatic hydrocarbons with GIMIC and NICS, and reinforced previous conclusions regarding the inadequacy of NICS to describe aromaticity in fused arene compounds. Recently, Baryshnikov *et al.*¹⁷⁰ employed GIMIC to investigate the aromaticity of hetero[8]circulenes, including quantitative values of ring current intensities (Figure 17).

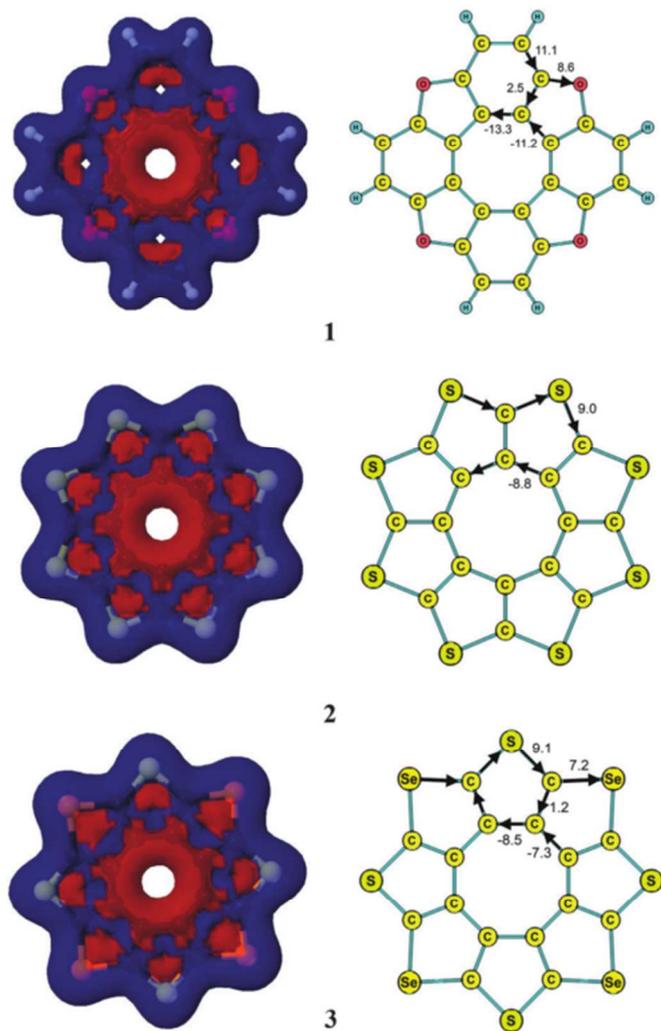


Figure 17. The ring current densities (left) and ring current strengths (right) for each bond in hetero[8]circulene molecules. (Red and blue colors denote the paratropic and diatropic ring currents, respectively). Reproduced from Reference 170 with permission from The PCCP Owner Societies.

As with NICS, CD maps have also been used to study the aromaticity of all-metal clusters and inorganic rings. The Fowler group studied the Al_4^{-2} ion extensively over a number of years. Using the ipsocentric approach, they found diamagnetic ring currents stemming from the σ framework.¹⁷¹ Though this conclusion seemed to be in contradiction to NICS and GIMIC results, which indicate significant π aromaticity, Havenith *et al.* later resolved this contradiction.¹⁷² However, it is important to recall Lazzarotti's criticism¹⁰⁹ regarding the extension of the term "aromaticity" beyond the organic world and into inorganic. If the term is used too widely, it loses its meaning and significance as a classifying characteristic.

A picture is worth a thousand words, and this is indeed true for current density analysis. A single CD map reveals a wealth of information of the behavior of the induced current within a studied compound. Yet, CD methods are not without drawbacks. In fact, there are several fundamental disadvantages of CD methods.

As Lazzarotti emphasized,¹⁷³ one major disadvantage is the difficulty of obtaining quantitative results. Different compounds may generate similar maps, which misleadingly indicates their diatropicity to be the same, though it is in fact different.

The current density is a vector field, thus it can only be represented graphically by choosing a sectional plane. This begs the question: at which height should two compounds be calculated in order to compare them meaningfully?

The vector field is dependent upon the orientation of the molecule in the magnetic field. CD maps have been calculated almost exclusively for planar compounds, because only in those cases is the orientation of the external field unambiguous. For non-planar molecules, this remains a problem.

Most CD methods are not easily accessed, as they aren't implemented in popular commercial software. They require additional software, such as the SYSMO¹⁷⁴ (for the ipsocentric methods) or GIMIC¹⁵⁸ programs. These programs also require much more user expertise, and are often modified by the user to meet specific requirements. It is noted that GIMIC has been implemented in TurboMole¹⁷⁵ and plots are generated with additional software, such as Jmol.¹⁷⁶ ACID can be implemented in Gaussian.

Summary and outlook

The study of aromaticity has come a long way since Kékulé's hypothesis of the circular movement of double bonds. It seems that in the last two to three decades the fundamental research of aromaticity has come to rely mainly on magnetic properties, concentrating on the fundamental aspects of aromaticity and on the development and application of tools for its qualitative and quantitative description. With the progress of computers and software, the field has become more and more theoretical- and computation-based. Indeed, unless new experimental tools are developed, it appears that this field will soon become entirely theoretical-computational.

As this review suggests, there are many methods and tools available for the study of aromaticity. From user-friendly single-point dissected NICS methods, which can be handled by the most popular QM package – Gaussian – with the NBO⁹³ procedure or NICS-scan procedures¹⁷⁷ to more specialized CDA methods. Each of the approaches has its “pros” and “cons”, and it seems that a comprehensive picture can be obtained only by the combined use of a few of the methods. All of the methods are based on approximations of different types, and it is of extreme importance to bear this in mind when applying them, so that the researcher does not reach incorrect conclusions and over-interpretations.

Where is this field going? There is a Hebrew phrase that states that “since the destruction of the holy temple, the prophecy was given to babes and fools”. As the authors of this paper do not belong to the former group, nor – hopefully – to the latter group, we will not risk predicting the future. We estimate, however, that the growth of the field will proceed in two directions. One is the development of better theories and user-friendly computational tools, such that every organic chemist will be able to obtain information about the aromatic properties of any (or most) systems. The second is the application of the knowledge and understanding that has been gained in the fundamental research, for designing useful reactions, systems and even devices.

Acknowledgements

R.G.P. thanks the Schulich Department of Chemistry for a Ph.D. Fellowship. A.S. thanks the Israeli Science Foundation (grant no. 1485/11) for financial support.

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