Visualisation of Chemical Shielding Tensors (VIST) to Elucidate Aromaticity and Antiaromaticity

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Aromaticity is a central concept in chemistry, pervading areas from biochemistry to materials science. Recently, chemists also started to exploit intricate phenomena such as the interplay of local and global (anti)aromaticity or aromaticity in non-planar systems and three dimensions. These phenomena pose new challenges in terms of our fundamental understanding and the practical visualisation of aromaticity. To overcome these challenges, a method for the visualisation of chemical shielding tensors (VIST) is developed here that allows for a 3D visualisation with quantitative information about the local variations and anisotropy of the chemical shielding. After exemplifying the method in different planar hydrocarbons, we study two non-planar macrocycles to show the unique benefits of the VIST method for molecules with competing pi-conjugated systems and conclude with a norcorrole dimer showing clear evidence of through-space aromaticity. We believe that the VIST method will be a highly valuable addition to the computational toolbox.

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Visualisation of chemical shielding tensors (VIST) to elucidate aromaticity and antiaromaticity

Felix Plasser[a] and Florian Glöcklhofer[b]

Abstract: Aromaticity is a central concept in chemistry, pervading areas from biochemistry to materials science. Recently, chemists also started to exploit intricate phenomena such as the interplay of local and global (anti)aromaticity or aromaticity in non-planar systems and three dimensions. These phenomena pose new challenges in terms of our fundamental understanding and the practical visualisation of aromaticity. To overcome these challenges, a method for the visualisation of chemical shielding tensors (VIST) is developed here that allows for a 3D visualisation with quantitative information about the local variations and anisotropy of the chemical shielding. After exemplifying the method in different planar hydrocarbons, we study two non-planar macrocycles to show the unique benefits of the VIST method for molecules with competing (anti)aromaticity and the interplay of ground-state antiaromaticity with triplet excited states. Moreover, application of Clar’s sextet theory for molecules with competing (anti)aromaticity provides a powerful way to control local aromaticity and antiaromaticity. Possible applications include mechanoresponsive materials.

Introduction

The concept of aromaticity has intrigued chemists for over 200 years[1] and is a fundamental ingredient in our understanding of the properties and reactivity of molecules. Aromatic molecules play central roles in many areas of chemistry, such as organic chemistry, biochemistry, photochemistry, and molecular materials science. More recently, chemists also started to consider local aromatic effects and antiaromaticity in the design of organic materials offering promising applications based on fascinating chemistry. The field of singlet fission, [2] as one prominent example, has been invigorated by both ideas, and the modulation of local aromaticity via the insertion of heteroatoms[3,4] and the interplay of ground-state antiaromaticity with triplet excited-state aromaticity[5–7] have lead to a new push in the quest for molecules with the desired energies of their singlet and triplet excited states. Moreover, application of Clar’s sextet theory[8] to control local aromaticity provides a powerful way of tuning biradical character, thus, opening the route to a range of optoelectronic applications.[9–12]

A new and exciting frontier is opened in terms of macrocycles and larger \( \pi \)-conjugated systems, in which local and global (anti)aromaticity can both play a role. Here, (anti)aromaticity can be studied in systems as diverse as nanographenes,[13,14] porphyrin nanorings,[15,16] carbon nanobelts,[17] cyclocarbon,[18] cycloparaphenylenes,[19] cycloparaphenylmethine,[20] paracyclophanetetraene,[21] norcorrole[22,23] and other porphyrinoids.[24,25] Several of these systems are interesting due to their remarkable capacity to stabilise multiply charged ions[19] making them promising candidates for organic battery electrodes.[21,26,27] Excited-state (triplet) aromaticity also being investigated,[30–33] as well as three-dimensional aromaticity in stacked systems,[34] cyclophanes,[35] \( \pi \)-conjugated cages,[36] and borane cages.[37] Finally, homoaromaticity provides yet another fascinating field of non-standard aromaticity,[38–41] with potential applications in mechanoresponsive materials.[40]

Considering the ubiquity of aromaticity in chemistry and its diverse appearances, there has been a strong push toward the development of methods to visualise and quantify aromaticity in different instances, many of which are related to the characteristic signals of (anti)aromatic systems in nuclear magnetic resonance (NMR) spectroscopy. Popular methods rely on current densities, such as the anisotropy of the induced current density (ACID)[42] or the gauge including magnetically induced current (GIMIC).[43] A prominent quantitative measure for aromaticity is provided by the nucleus-independent chemical shifts (NICS) corresponding to a nuclear magnetic resonance (NMR) experiment performed at a virtual nucleus at the centre of an aromatic ring. NICS values can be visualised after computing them on a grid around the molecule of interest[45–48] and several recent applications present 1D scans, 2D contour plots or even 3D isosurfaces of the isotropic NICS values, e.g. to visualise local aromatic and antiaromatic parts of larger molecules,[6,22,35,49] to represent Clar sextets in condensed hydrocarbons,[50] or to study interactions in excimers.[51] These visualisations are almost exclusively based on isotropic NICS values. However, new challenges come into play in macrocycles and multi-ring systems where several ring-currents in different planes interact, possibly resulting in strong magnetic anisotropy. To overcome this problem it would be greatly beneficial to have a method for the visualisation of the full underlying shielding tensor.

The purpose of this work is to develop such a method, denoted VIST (visualisation of chemical shielding tensors). VIST will allow us to visualise local variations in aromaticity and antiaromaticity, and

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antiaromaticity in the context of the molecular structure while also providing insight into the anisotropy of the chemical shielding. Briefly spoken, the method proceeds by computing the chemical shielding tensor at a given point in space, computing its principal axes via a diagonalisation, and showing them as a local coordinate system. The method is sketched in Fig. 1. In this example, there is one strong deshielded (antiaromatic) component shown in red and two weaker shielded (aromatic) components shown in blue. Any one of these tensor components relates to the ring currents in a plane perpendicular to it. In this example, there is one strong deshielded (antiaromatic) component shown in red and two weaker shielded (aromatic) components shown in blue. Any one of these tensor components relates to the ring currents in a plane perpendicular to it.

\[ \sum_{\beta \in \{x,y,z\}} \sigma_{\gamma \beta} q_{\beta}^{(i)} = t^{(i)} q_{\gamma}^{(i)} \quad i \in \{1,2,3\} \]

For visualisation, we construct a local coordinate system oriented according to the eigenvectors \( q^{(1)} \) and visualise the three components as dumb-bells whose size and length depend on the absolute value of the associated eigenvalue \( |t^{(i)}| \) and whose color depends on the sign (blue or red), see Fig. 1. Through encoding the eigenvectors and eigenvalues in the representation, we are able to represent the full information given in the 3 × 3 tensor graphically. A direct connection to the quantitative information contained in the NICS values is given by noting that in analogy to Eq. (2) the NICS value is a third of the sum of the three eigenvalues according to

\[ \text{NICS} = -\sigma_{\text{iso}} = -\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}). \]

Note that the chemical shielding and NICS are thus equivalent except for the sign and we shall use both terms interchangeably.

Visualisation of the shielding is not straightforward considering that it is given as a non-symmetric 3 × 3 tensor containing 9 independent values at every point in space. Whereas scalar-valued functions can be represented in 3D space via iso-surfaces and vector-valued functions via arrows, it is necessary to construct a more involved representation for a tensor-valued function. Here, we suggest to do so by constructing the principal axes of the chemical shielding tensor as its eigenvectors in analogy to the principal axes of the moment of inertia. The eigenvectors \( q^{(1)}, q^{(2)}, q^{(3)} \) and eigenvalues \( t^{(1)}, t^{(2)}, t^{(3)} \) are given as

\[ \sum_{\beta \in \{x,y,z\}} \sigma_{\gamma \beta} q_{\beta}^{(i)} = t^{(i)} q_{\gamma}^{(i)} \quad i \in \{1,2,3\} \]

\[ \text{NICS} = -\sigma_{\text{iso}} = -\frac{1}{3}(t^{(1)} + t^{(2)} + t^{(3)}). \]

Finally, we want to point out that the shielding tensor is in general represented by a non-symmetric matrix, which gives rise to two technical points to consider: (i) the fact that the left and right eigenvectors are not the same and (ii) the occurrence of complex eigenvalues. Both points are discussed in Sec. S1 of the supporting information.

We have implemented the VIST method within the TheoDORE wavefunction analysis package\(^\text{54–56}\) and a first version of the code is scheduled to be released within TheoDORE 2.4. See Sec. S2 for more information on the programs and methods used.

**Results and Discussion**

**Benzene**

Shielding tensors for benzene were computed at various positions around the molecule to examine how the shielding varies...
with the position, illustrating the basics of the VIST method (Fig. 2). The chemical shielding at the centre of the ring, also denoted NICS(0), is presented in Fig. 2 (a). The tensor representation shows a dominant out-of-plane component (-13.3 ppm) along with two smaller in-plane components (both -6.7 ppm), which average to an overall isotropic NICS(0) value of -8.9 ppm. Due to the high symmetry present, the out-of-plane eigenvalue is equivalent to the NICS(0)$_{zz}$ value, which has been reported as -13.2 ppm elsewhere. Indeed, when considering the NICS(0) values in Fig. 3 (b), we find that the outer rings (A) experience significantly enhanced shielding when compared to the inner ring (B). Interestingly, the out-of-plane component of NICS(0) computed at the inner ring almost vanishes. A comparison to benzene shows that the isotropic NICS(0) value at the outer rings is slightly higher for phenanthrene than benzene (-9.2 vs -8.9 ppm) but that the out-of-plane component is clearly lower (-11.7 ppm vs -13.3 ppm).

To reduce any contributions from the $\sigma$-system, we proceed to the NICS(1) tensors, as shown in Fig. 3 (c). These have strong out-of-plane components in all three rings, representing strong in-plane aromaticity and, again, the outer rings are notably enhanced. The isotropic NICS(1) values as well as the individual tensor components of the side rings are very similar to benzene [Fig. 2 (c)] with the exception that the eigenvectors corresponding to the smaller contributions are slightly tilted out of plane.

For comparison, we also want to show a different representation of aromaticity, which proceeds by computing the current density induced by a magnetic field perpendicular to the molecular plane and dividing the current into diatropic and paratropic contributions, which can roughly be understood as the currents giving rise to diamagnetic shielding and paratropic deshielding.
Figure 3: Analysis of local aromaticity in phenanthrene: (a) molecular structure with Clar sextets highlighted in blue; 3D visualisation of the chemical shielding tensors (VIST, see Fig. 2 for details) computed at (b) the centre of each ring and (c) 1Å above the plane. NICS values (in ppm) are reported for the outer (A) and inner (B) rings. The isosurface of the current density modulus induced by a magnetic field in z-direction is shown in (d) (cutoff 0.1 a.u., blue - diatropic, red - paratropic).

respectively. Diatropic and paratropic ring currents are shown in Fig. 3 (d) in blue and red. In line with previous results, one finds diatropic ring currents outside of the bonds, extending over σ- and π-orbitals, and paratropic currents inside, deriving mainly from σ-orbitals. The diatropic currents (blue) dominate, explaining the net shielding seen in Fig. 3 (b) and (c). Closer inspection shows that the main paratropic contributions are located within the inner ring, explaining why shielding is reduced there, in particular for the NICS(0) tensors. The effect of these σ-contributions is reduced once one moves out of the molecular plane, explaining why strong shielding is obtained for all NICS(1) tensors.

In summary, we found that for a simple system like phenanthrene the isotropic NICS values already reflect the correct trends in terms of its variations in local aromaticity. However, the VIST method provides a detailed and intuitive representation of the individual shielding components, including the somewhat surprising result that the out-of-plane component at the inner ring almost vanishes. We have also highlighted that the visualisation of the current density can provide complementary information to the shielding tensors, thus, providing a combined strategy for illuminating intricate details of aromatic ring currents.

Cyclobuta[l]phenanthrene — antiaromaticity and Baird aromaticity

Whereas the previous two molecules were aromatic, we want to proceed by illustrating how the VIST method can be used particularly effectively to study the interplay of local aromaticity and antiaromaticity and their modulation via the electronic spin state. For this purpose, we add a cyclobutadiene (CBD) ring to phenanthrene to produce the cyclobuta[l]phenanthrene molecule. This molecule was reported as a potential singlet fission chromophore, owing to its low-energy first triplet state (<1eV) despite maintaining a large excitation energy of its first singlet excited state (>2eV).\textsuperscript{6} The low triplet energy was explained by the combination of ground-state antiaromaticity and triplet-state Baird aromaticity of the CBD ring and we shall illustrate these phenomena below.

The molecular structure of cyclobuta[l]phenanthrene is shown in Fig. 4 (a), highlighting its aromatic Clar sextets in blue along with its antiaromatic CBD ring in red. The NICS(0) tensors of the singlet ground state presented in Fig. 4 (b) have a striking appearance with a strongly dominant out-of-plane antiaromatic (red) component on the CBD ring. The associated eigenvalue of 131.8 ppm is far higher in magnitude than any shielding value found in the above examples. Moving to the NICS(1) tensors in Fig. 4 (c) we find that antiaromaticity is still clearly visible but that the magnitude of the deshielding is strongly reduced (from 132 to 73 ppm for the dominant eigenvalue), a result also obtained for an isolated CBD molecule.\textsuperscript{58,61}

When viewing the phenanthrene part of the molecule, we find that the shielding tensors are only slightly perturbed as compared to isolated phenanthrene (Fig. 3).

Following Baird’s rule,\textsuperscript{28} one expects the four-membered CBD ring to exhibit aromaticity in its lowest triplet state. To examine this hypothesis, we have performed computations on this state. We start the discussion with the difference density between singlet and triplet to describe the electronic rearrangement involved. Fig. 4 (d) shows that the difference density is located on the CBD ring and, specifically, that the transition from the singlet to the triplet means a reduction (orange) in density along the bonds that are indicated as double bonds in Fig. 4 (a) and an enhancement (purple) in density on the other two bonds, resulting in an overall more even charge distribution around the CBD ring.

The change from singlet to triplet has a profound impact on the magnetic shielding, as shown in Fig. 4 (e, f), most importantly by eliminating the strongly deshielded component perpendicular to the CBD ring (C). Viewing the NICS(0) tensors [Fig. 4 (e)], we find that the CBD ring remains slightly deshielded while also the central 6-membered ring (B) obtains a slightly deshielded contribution. The z-components of the shielding tensors on the outer rings (A) are also reduced in
Paracyclophanetetraene – interplay of local aromaticity and global antiaromaticity in a macrocycle

Paracyclophanetetraene (PCT) is a non-planar macrocycle with competing \(\pi\)-conjugated systems aligned in different planes and, hence, a particularly challenging case for the purposes of visualising and quantifying its local variations in (anti)aromaticity. The macrocycle, as shown in Fig. 5 (a), features a \(\pi\)-conjugated perimeter of 24 \([4n]\) \(\pi\)-electrons as well as four slightly twisted phenylene subunits with 6 \([4n+2]\) \(\pi\)-electrons, each. In the neutral state, the macrocycle is formally antiaromatic but, in practice, was reported to not exhibit any measurable antiaromatic properties.\(^{21}\) Twofold reduction, on the other hand, was reported to create a globally aromatic macrocyclic system of \([4n+2]\) \(\pi\)-electrons whose enhanced stability renders PCT a promising new material for sodium-ion battery anodes.

Figure 4: Analysis of local (anti)aromaticity in the lowest singlet and triplet states of cyclobuta[\(l\)]phenanthrene: (a) molecular structure with Clar sextets highlighted in blue and the antiaromatic ring in red; 3D visualisation of the chemical shielding tensors (VIST, see Fig. 2 for details) computed at (b)/(e) the centre of each ring and (c)/(f) 1 Å above the plane for the singlet/triplet; (d) difference density between singlet and triplet. NICS values (in ppm) are reported for the A, B, C positions as shown in (a).

magnitude, yielding a NICS\(_{zz}(0)\) value of only -3.2 ppm. Interpreting the NICS(0) contributions is not straightforward as it is not clear how to separate between the contributions from the \(\pi\)-electrons in the individual rings as well as the \(\sigma\)-electrons. Therefore, we also present the NICS(1) contributions to get a different viewpoint [Fig. 4 (f)]. Interestingly, the NICS(1) tensors all show pronounced aromaticity for the CBD ring as well as the outer phenanthrene rings. It is noteworthy here that the values for the outer rings in phenanthrene (A) are almost unaltered between the singlet and triplet states, i.e. when comparing panels (c) and (f), suggesting that their \(\pi\)-electrons are not strongly perturbed by the excitation. The central ring (B), on the other hand, experiences a significant decrease in aromaticity. In summary, Fig. 4 (f) suggests to view the electronic structure of cyclobuta[\(l\)]phenanthrene in its triplet state as a combination of a Baird aromatic quartet with two Clar sextets (cf. Ref. 62).

Figure 5: Analysis of local (anti)aromaticity in paracyclophanetetraene: (a) molecular structure; 3D visualisation of the chemical shielding tensors (VIST, see Fig. 2 for details) for (b) the neutral and (c) the dianion – NICS values (in ppm) are reported for the phenylene ring (A), the centre (B), and side (C) of the macrocycle; ACID plots for (d) the neutral and (e) the doubly reduced form (isovalue 0.05).

Chemical shielding tensors were computed at three positions
within the macrocycle: 1 Å off the plane of one of the phenylene rings (A), at the centre of the macrocycle (B), and on the side next to the double bond (C). Starting with the centre position (B), we find a deshielded component of 11.0 ppm along with two shielded components (-4.8 ppm) averaging to an isotropic NICS value close to zero. Moving closer to the side of the macrocycle (C) we find somewhat stronger deshielding (25.9 ppm), supporting the presence of global antiaromaticity for the macrocycle. However, it should be pointed out that part of the deshielding derives from diatropic currents in the benzene rings as shown in Fig. 53, thus, indicating only weak antiaromatic character in line with the experimental observations.

Next, we test the hypothesis of local aromaticity on the phenylene rings. For this reason, we have computed the NICS(1) tensor for one of the phenylene rings shown on the left in Fig. 5 (b). The tensor is tilted to be perpendicular to the phenylene ring but otherwise possesses a similar shape to the NICS(1) tensor of an isolated benzene molecule [Fig. 2 (b)] with only slightly reduced aromaticity (-24.2 vs -29.5 ppm for the dominant eigenvalue). This highlights that the local aromaticity in the phenylene rings is largely unperturbed by the macrocycle. Note that the tilt seen in Fig. 5 (b) represents a non-trivial combination of all the tensor components and would be difficult to comprehend without the VIST method.

The dianion shown in Fig. 5 (c) has a dramatically different appearance compared to the neutral state. Strong aromaticity (blue) perpendicular to the plane of the macrocycle is found for all three positions probed. The dominant eigenvalues obtained for positions B and C, -38.7 and -52.1 ppm, are even higher than the NICS(1)zz eigenvalue for benzene, shown in Fig. 2 (b). Viewing the phenylene position (A) one finds somewhat reduced shielding values and a tilt of the main component with respect to Fig. 5 (b) making it almost perpendicular to the plane of the macrocycle. These findings indicate that the local aromaticity of the phenylene ring is perturbed to allow for enhanced global aromaticity.

For comparison we also want to show the ACID plots of the neutral and doubly reduced form, Fig. 5 (d.e). The isosurfaces shown represent the delocalised electrons whereas the small arrows represent the direction of the current if a magnetic field is applied in z-direction. The ACID plots show that electron delocalisation extends over all carbon atoms in the macrocycle in both states shown and that there is more delocalisation in the dianion than in the neutral state. Upon closer inspection, one finds arrows going in clockwise direction in Fig. 5 (e), representing the diatropic ring current that is responsible for the strong shielding seen in Fig. 5 (c). It is not possible to identify the paratropic ring currents in panel (d) that are responsible for the deshielding found in the neutral state. It is even challenging to locate the local diatropic ring currents in the phenylene units that give rise to their local aromaticity, which is unambiguously seen in Fig. 5 (b).

In summary, Fig. 5 underscores the dramatic changes PCT undergoes upon twofold reduction, explaining its remarkable redox properties. The ACID plots were useful for highlighting the overall electron distribution but the new VIST method provided a direct representation of the remarkable changes in electronic structure following the switch from local to global aromaticity.

**Cycloparaphenylene**

Cycloparaphenylene (CPP), composed of phenylene units connected in para-position, are an intensively investigated class of conjugated macrocycles. CPPs are attracting interest due to their unique optoelectronic properties in combination with their rich host-guest chemistry providing a promising basis for applications from solid-state nanomaterials to biological imaging. When viewing the global properties of CPP macrocycles, every phenylene unit contributes 4 π-electrons to the macrocyclic π-conjugated pathway, meaning that any [n]CPP (where n represents the number of phenylene units) has 4n electrons in its π-conjugated pathway and is, thus, expected to be antiaromatic. Two-fold oxidation or reduction creates global aromaticity, in line with the discussion on PCT in the last section.

An analysis of the neutral molecule is presented in Fig. 6 (a). Chemical shielding tensors were computed along a line going from the centre of one phenylene ring to the centre of a phenylene ring on the opposite side. Inside the macrocycle, one finds a slight deshielding (red) of up to 3.7 ppm in the out-of-plane direction. However, this is compensated by in-plane shielding and the isotropic NICS values inside the ring are all negative, in agreement with Ref. 19. When chemical shielding tensors are computed close to a phenylene ring, as shown on the left, one finds that they are strongly tilted as these now represent local aromaticity in the phenylene rings, which lie perpendicular to the plane of the macrocycle.

Next, we present computations on the dication, which was reported to exhibit strong global aromaticity. Indeed, viewing Fig. 6 (b), we find strong shielded (blue) tensor components perpendicular to the plane of the macrocycle. At the centre of the ring, we find an out-of-plane NICS component of -36.4 ppm, which is similar to the dianion of PCT as shown in Fig. 5 (c), and slightly higher values (up to -51.6 ppm) are obtained closer to the phenylene rings. Viewing the contributions to the left and right of the phenylene ring shown on the left in Fig. 6 (b), one finds that the local aromaticity on the phenylene ring is clearly reduced as opposed to the neutral form, suggesting that the redox chemistry of [8]CPP can be described in terms of a switch between local and global aromaticity similarly to PCT.

Fig. 6 (a) shows that there is no appreciable global antiaromaticity for [8]CPP at its ground state optimised geometry. However, it is interesting to probe whether [8]CPP has a propensity toward antiaromaticity in principle. For this purpose, we have performed computations of the neutral system at the dication geometry. The dication has shorter CC bonds (1.45 vs 1.48 Å) and reduced torsion angles (7° vs 30°) between adjacent phenylene rings, allowing for enhanced conjugation throughout the macrocycle. The resulting shielding tensors, shown in Fig. 6 (c), highlight that, indeed, the dication geometry leads to enhanced antiaromaticity in the neutral system.
with NICS components up to 10.3 ppm. We are, thus, left to conclude that the neutral molecule possesses a propensity towards antiaromaticity due to its macrocyclic $4n \pi$-electron system but that it has sufficient conformational flexibility to adopt a geometry where antiaromaticity is minimised.

Finally, viewing the dianion in Fig. 6 (d), we find that its chemical shielding structure looks very similar to Fig. 6 (b), highlighting that it exhibits global aromaticity just as the dication geometry.

Figure 7: Analysis of local (anti)aromaticity in a stacked norcorrole dimer: Molecular structures of (a) the monomer and (b) the dimer; 3D visualisation of the chemical shielding tensors (VIST, see Fig. 2 for details) for (c) the monomer and (d) the dimer. NICS values (in ppm) are reported at the positions indicated in (a).

**Norcorrole dimer – through-space aromaticity**

Ni(II) norcorrole [Fig. 7 (a)] is a prominent antiaromatic compound. Its $[4n] \pi$-electron system cannot escape planarity due to the rigidity of the molecular structure, explaining why strong antiaromaticity is indeed observed in this molecule. Bulky mesityl substituents can be attached to the conjugated core of Ni(II) norcorrole to improve its stability, but the compound is comparatively stable also without these substituents, despite the antiaromaticity. The comparatively high stability of Ni(II) norcorrole makes it an ideal molecule to study stacking interactions between antiaromatic $\pi$-conjugated systems and the ensuing emergence of three-dimensional aromaticity. Initially, stacking of flexibly linked Ni(II) norcorrole complexes was investigated, followed by a more recent report of a rigid cyclophane composed of two Ni(II) norcorrole units and two bithiophene linkers. These studies highlighted the importance of through-space currents connecting the two macrocycles.

Within this work, we study the Ni(II) norcorrole complex reported in Ref. 35 but with removed bithiophene linkers, as shown in Fig. 7 (b). Shielding tensors were computed at three different positions, as shown in Fig. 7 (a): 1 Å above the outer 5-membered ring (A), 1 Å above the 6-membered ring (B), and at the centre of the complex, halfway between the two Ni-atoms (denoted Ni). Starting with the Ni(II) norcorrole monomer [Fig. 7 (c)] we find pronounced antiaromaticity when measured at the Ni and B positions with dominant eigenvalues...
of 185 and 155 ppm, respectively, which are higher than any of the values seen in the above examples. Interestingly, the 5-membered ring (A) shows significantly reduced antiaromaticity. This reduction in deshielding for the 5-membered ring, which was also seen in Ref. 23, has been explained in the sense that antiaromatic currents are only present on the inner part of the ring and that norcorrole possesses an aromatic pathway on the perimeter.\(^{22}\)

To study the effect of stacking between two norcorrole units, we have added a second ring to the system but, otherwise, left the geometry of the first ring and the positions of the chemical shielding tensors unchanged. The striking impact of the second ring is illustrated in Fig. 7 (d): The antiaromaticity disappears for positions A and B and is strongly reduced at the centre of the complex.

Viewing only the isotropic NICS value at the centre of the ring (1.2 ppm) it might be tempting to jump to the conclusion that no relevant shielding effects are present. However, the VIST plot immediately shows that this is incorrect and that the isotropic value is obtained as an average of strong out-of-plane deshielding (49 ppm) in combination with in-plane the isotropic value is obtained as an average of strong out-of-plane deshielding (49 ppm) in combination with in-plane

VIST also provides an expedient route to illustrate the chemical shielding in unprecedented clarity. VIST is, thus, particularly useful for large, non-planar molecular systems where it can be exceedingly difficult to obtain the required information otherwise. VIST also provides an expedient route to illustrate the influence of different electronic charge and spin states on (anti)aromaticity.

Within this work, the basic properties of the VIST method could be illustrated in the case of planar polycyclic hydrocarbons. Starting with benzene, we investigated how the shape of the shielding tensor changes at different positions surrounding the molecule. Moving to phenanthrene, we illustrated local variations in aromaticity in this molecule and discussed the shielding tensors in the context of the magnetically induced currents. For cyclobuta[l]phenanthrene the interplay of local aromaticity and antiaromaticity in its singlet state and the emergence of Baird aromaticity in its triplet was studied.

Moving to non-planar macrocycles with competing aromatic and antiaromatic systems aligned in different planes, we were able to illuminate the full power of the VIST method. Starting with PCT, we highlighted the combination of local aromaticity and weak global antiaromaticity in its ground state and a switch to global aromaticity in its doubly reduced state. A similar picture was obtained for [8]CPP, which exhibits pronounced aromatic character in its doubly oxidised and reduced states. The VIST method, thus, can provide a clear explanation of the remarkable redox properties of both macrocycles. Finally, studying the stacking between two norcorrole molecules, we showed how strong in-plane antiaromaticity in Ni(II) norcorrole was replaced by weaker in-plane antiaromaticity in combination with through-space aromaticity upon stacking.

Practically, VIST builds on the computation of NICS values and can, thus, be carried out whenever NICS values are available. Moreover, it is readily integrated into existing tools used for the visualisation of molecular structures and electron densities. Therefore, we are convinced that VIST constitutes a powerful but also flexible and lightweight computational tool and provides a much-needed extension to the toolbox of chemists studying (anti)aromaticity or using it in their molecular design.

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Keywords: aromaticity, antiaromaticity, chemical shift, hydrocarbons, \(\pi\)-conjugated systems

Conclusions

We can conclude that the visualisation of chemical shielding tensors (VIST) presented in this work is a highly valuable method to elucidate aromaticity and antiaromaticity in molecules. The VIST method shows the chemical shielding tensor at various points in space around a molecule, thus, allowing to represent the local variations and anisotropy of the chemical shielding in unprecedented clarity. VIST is thus, particularly useful for large, non-planar molecular systems where it can be exceedingly difficult to obtain the required information otherwise. VIST also provides an expedient route to illustrate the influence of different electronic charge and spin states on (anti)aromaticity.

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A method for the visualisation of chemical shielding tensors (VIST) is developed, which provides a graphical representation of aromaticity and antiaromaticity, their local variations and anisotropy. The method provides unique insight into fascinating phenomena such as the interplay of aromaticity and antiaromaticity in macrocycles with competing \( \pi \)-conjugated systems.

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Supporting Information

for

Visualisation of chemical shielding tensors (VIST) to elucidate aromaticity and antiaromaticity

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January 30, 2021

Contents

Section S1 - Left eigenvectors and complex eigenvalues 2
Section S2 - Computational Details 3
Section S3 - Benzene 3
Section S4 - Paracyclophanetetraene 4
Section S5 - Norcorrole dimer 4
Section S1 - Left eigenvectors and complex eigenvalues

The shielding tensor is in general represented by a non-symmetric matrix, which gives rise to two technical issues, which we shall discuss briefly in the following: (i) the presence of left eigenvectors and (ii) the occurrence of complex eigenvalues. In Eq. (3) of the main manuscript we have considered the right eigenvectors of the chemical shielding tensor and we will use these in the following unless noted otherwise. Alternatively, it would be possible to do the same decomposition using the left eigenvectors

$$\sum_{\gamma \in \{x,y,z\}} t^{(i)}_{\gamma} \sigma_{\gamma \beta} = t^{(i)}_{\beta} l^{(i)} \quad i \in \{1, 2, 3\}$$ (S1)

This would yield the same eigenvalues $t^{(i)}$ as Eq. (3), considering that they are determined as the roots of the same characteristic polynomial, but it would generally produce different principal axes. Note that the two equations differ in the sense that the summation in Eq. (3) goes over the components of magnetic field $B_{\beta}$ whereas the summation in Eq. (S1) is performed with respect to the formal nuclear moments $\mu_{\gamma}$. It is not a priori clear which representation is better. In practice, we have found that the representations have a similar appearance only that the left eigenvectors are a bit tilted with respect to the right ones. To exemplify this, we show the right and left eigenvectors of the shielding tensors of anthracene in its singlet ground state in Fig. S1 (b,c) and (d,e), respectively. First, it is noted that the left eigenvalues are the same as the right eigenvalues meaning that the length of the axes and size of the spheres is the same. In the case of the NICS(0) tensors, we also find that, due to symmetry reasons the left eigenvectors are exactly the same as the right ones. When viewing the NICS(1) tensors we find that the left eigenvectors are somewhat tilted with respect to the molecular plane but that they, otherwise, have a similar appearance to the right eigenvectors. We found the same conclusion also for other examples: the left eigenvectors are similar to the right eigenvectors with the exception of being slightly tilted. We, thus, continue by viewing only the right eigenvectors and suggest using these for future applications.

![Figure S1](image)

**Figure S1**: Analysis of local aromaticity in anthracene: (a) molecular structure with Clar sextet highlighted in blue; 3D representation of the chemical shielding tensors using the right eigenvectors computed at (b) the centre of each ring and (c) 1Å above the plane; (d) and (e) same as above using the left eigenvectors. NICS values (in ppm) are reported for the outer and inner rings.

Furthermore, we want to discuss the case where one of the eigenvalues, e.g. $t^{(1)}$, is a complex number. In this case, we use a mathematical formalism similar to the construction of two-dimensional real representations of cyclic symmetry groups. Due to the fact that the $\sigma$-matrix is real, it follows that if $t^{(1)}$ is complex, also its complex conjugate $t^{(1)*}$ is an eigenvalue and that the associated eigenvector is the complex conjugate of $\vec{q}^{(1)}$. In summary, we can write

$$t^{(2)} = t^{(1)*} \quad \vec{q}^{(2)} = \vec{q}^{(1)*}$$ (S2)

Noting this relation, we use the following three vectors as a basis for the coordinate system: $\text{Re}(\vec{q}^{(1)}), \text{Im}(\vec{q}^{(1)}), \vec{q}^{(3)}$ where Re and Im denote the real and imaginary parts of the vectors. The associated diagonal matrix elements are $\text{Re}(t^{(1)}), \text{Re}(t^{(1)}), t^{(3)}$ noting that these conserve the trace in analogy to Eq. (4) of the main text, i.e.
\[
\sigma_{\text{iso}} = \frac{1}{3} \left( \text{Re}(t^{(1)}) + \text{Re}(t^{(1)}) + t^{(3)} \right)
\]  

(S3)

Section S2 - Computational Details

Chemical shielding tensors were computed in Gaussian 09 \(^1\) using the PBE0 functional \(^2,3\) along with the def2-SVP basis set \(^4\) using gauge-including atomic orbitals \(^5\) and applying tight SCF convergence criteria. Calculations on the singlet (triplet) states were performed using restricted (unrestricted) density functional theory. Molecular geometries of benzene, phenanthrene, cyclobuta[l]phenanthrene, PCT, and [8]CPP were optimised at the PBE0/def2-SVP level. Unless specified, shielding tensors were computed for geometries optimised for the respective spin/charge state. In the case of the stacked norcorrole dimer, the molecular geometry was taken from the crystal structure \(^6\) with removed bithiophene linkers. The same structure, but with one monomer removed, was used for the monomer calculation. The underlying research data (molecular geometries, Gaussian input/output files, and input scripts for VMD) are provided via a separate repository.\(^{14}\)

We have implemented the VIST method within the TheoDORE wavefunction analysis package.\(^7,8,9\) A first version of the code is scheduled to be released within TheoDORE 2.4. The visual molecular dynamics (VMD) \(^10\) program is used as a graphical backend for creating the tensor representations in connection with molecular structures and isosurfaces. The signed current density modulus \(^11\) of phenanthrene was computed using the GIMIC program.\(^12\) ACID plots for PCT used the ACID program.\(^13\)

In the VIST dumb-bell representation used, we consistently draw the length \(L\) of the axis and the radius \(R\) of the sphere as

\[
L = 2 \times 0.3 \sqrt{|t^{(i)}|} \quad R = 0.03 \sqrt{|t^{(i)}|}
\]

(S4)

where \(t^{(i)}\) is given in ppm and \(L\) and \(R\) are given in Å.

Section S3 - Benzene

\(\text{(a)}\) \(\text{(b)}\) \(\text{(c)}\) \(\text{(d)}\) \(\text{(e)}\) \(\text{(f)}\)

Figure S2: 3D visualisation of the chemical shielding tensors (VIST) in benzene. Negative (shielded/aromatic) contributions are shown in blue, positive (deshielded, antiaromatic) in red. Shielding tensors were computed at (a) the centre of the molecule, (b) 1 Å and (c) 2 Å above the plane; (d) at the centre of a bond, (e) 1 Å and (f) 2 Å above the bond. The electron density is shown in yellow (isovalue 0.1 a.u., encompassing about 60% of the total electron density).
Section S4 - Paracyclophanetetraene

\[
A: \text{NICS}(1) = -11.23 (-29.70/-2.26/-1.74) \\
B: \text{NICS}(0) = -0.31 (9.39/-5.16/-5.16) \\
C: \text{NICS}(0) = 1.31 (13.61/-12.18/2.49)
\]

Figure S3: 3D visualisation of the chemical shielding tensors (VIST) of four isolated benzene rings arranged according to the geometry of PCT in its singlet ground state. This figure shows that deshielding at positions B and C is also present for isolated benzene rings. Comparison to Fig. 5 shows that deshielding is enhanced in the full macrocycle.

Section S5 - Norcorrole dimer

Figure S4: 3D visualisation of the chemical shielding tensors (VIST) in the norcorrole dimer using alternative viewing angles highlighting the tilt and non-orthogonality of the principal axes at the outer positions.

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