PCCP

Physical Chemistry Chemical Physics

Accepted Manuscript

PCCP

Physical Chemistry Chemical Physics

rsc.li/pccp

Volume 19
Number 1
7 January 2017
Pages 1-896

ISSN 1463-9076

PAPER
H.-P. Loock et al.
Determination of the thermal, oxidative and photochemical
degradation rates of scintillator liquid by fluorescence EEM
spectroscopy.

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ARTICLE TYPE

Expanding Aromaticity Tests to Include Lowest-Lying Triplet Excited States and Charged and Heterocyclic Rings

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Aromaticity is a pivotal concept in chemistry arising from electron delocalization in closed-loop systems that confers extra energetic stabilization. Its direct observation is not possible, making its quantification challenging. To address this issue, several methods have been developed to quantify this non-observable property based on various physicochemical properties characteristic of these compounds. However, given the indirect nature of these measures, they do not always yield consistent or reliable aromaticity trends. Therefore, it is important to design tools that help identify which descriptors perform most effectively and put forward their weaknesses and strenghts. In a previous work (*J. Comput. Chem.* 2008, **29**, 1543–1554), we introduced a series of fifteen aromaticity tests that were used to analyze the advantages and drawbacks of a group of ten aromaticity descriptors. In this work, we propose to extent these initial tests of aromaticity with a series of thirteen tests related to excited state aromaticity, redox processes, and heterocyclic rings to evaluate the ability of twelve aromaticity descriptors. A comprehensive evaluation of the strengths and weaknesses of the analysed indicators of aromaticity reveals that electronic and magnetic indices perform most consistently, although the former show limitations when applied to oxidized species.

Introduction

Aromaticity is a crucial concept in the field of chemistry, not exempt from criticism.[1–10] Although no consensus exists on a precise definition, chemists continue to rely on this concept because of its fundamental role in the elucidation of some phenomena, such as the particular low reactivity, the interpretation of the molecular structure, and the spectroscopic and magnetic properties of an endless number of compounds.[11–13]

The never-ending ambiguity is caused by the fact that this property, although widely explored, it has never been directly observed.[14] The main problem in assessing the aromaticity of a molecule or its parts is that no property serves as a straightforward measure. However, the lack of a precise definition and the absence of a proper operator have not deterred chemists from developing various methodological approaches for its quantification.[12]

There is a general consensus on certain characteristic properties typically associated with aromatic moieties. The manifestation of these features is apparent in distinct chemical and phys-

ical behaviours, which are indicative of their enhanced kinetic and thermodynamic stability in comparison to their open-chain analogues. A molecule is classified as aromatic if it possesses a particular molecular and electronic structure. This characteristic structure is primarily manifested through the presence of a cyclic 2D or 3D moiety with delocalized electrons. Moreover, aromatic species have a tendency towards bond length equalization, and they exhibit distinctive spectroscopic and magnetic signatures. In particular, these compounds have been associated with an unusually high diamagnetic susceptibility, which Pauling,[15] London,[16] and Lonsdale[17] attributed to the induced ring current generated by the delocalized electrons, which results in abnormal chemical shifts.[18]

Given this situation, the assessment of the aromatic character is usually carried out indirectly through the measurement of the aforementioned common physicochemical properties that are indicative of aromatic character. Thus, even though aromaticity itself cannot be directly observed, chemists have managed to develop numerous indices for the quantification based on energetic, electronic, structural, magnetic, and reactivity measures.[12,19] These quantifiers provide an approximate measure of the central property of interest.

Even though this long-standing challenge has been addressed quite effectively, identifying a precise and universally accepted quantitative measure of aromaticity remains elusive. This dif-

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ficulty arises from the fact that aromaticity is linked to multiple molecular characteristics that are not necessarily interrelated.[20–24] The use of various aromaticity criteria derived from different properties has significant implications. As none of these approaches are free from ambiguity, there is often an absence of correlation among the values. Furthermore, the relative accuracy of each method remains uncertain, as no reliable references exist to assess and compare their effectiveness.

In light of the present circumstances, it is recommended to employ a range of indices from different origins. In front of all the results, when multiple indices based on different measures converge towards the same conclusion, one can confidently establish a solid outcome. Conversely, if the results are not in agreement, any final conclusion will be considerably weaker. Summarizing, while it is undoubtedly a significant challenge, and no unequivocal scale exists, initial indications can be obtained using different descriptors.[25–28]

Meanwhile, new aromaticity descriptors are frequently introduced in the literature.[29–31] The validation of a newly implemented quantifier is usually performed by means of correlation with a series of previously defined descriptors. As said before, the problem is that sometimes poor correlations are found among different indicators of aromaticity. Therefore, validation by comparison does not ensure the quality of a new descriptor. Given the limited reliability of current aromaticity quantifiers, there is a pressing need to develop a comprehensive toolkit that establishes the most suitable descriptors for different families of molecules.

A previous study had been conducted by some of us,[19] wherein the performance of a set of aromaticity descriptors was evaluated. In that work, fifteen tests of aromaticity were proposed to identify the most accurate aromaticity descriptors. The tests chosen describe simple situations in which the trends followed by the aromatic character of the different rings are widely accepted by the chemical community. In addition, they were chosen to facilitate a fast application to ensure that the testing set can be quickly and easily extended to incorporate any new quantifier. This approach allows one to readily assess the accuracy of these new indices, and additionally, one can also track whether any improvement has been achieved. By maintaining a straightforward system, we can easily keep our methodology up to date as the field evolves, allowing us to compare all available tools at any given time.

Back in 2008, aromaticity analyses of excited states were not commonly performed, which is why tests involving such states were not included. The present study extends that earlier work to systems not previously examined, including the aromaticity of lowest-lying triplet states, rings undergoing redox processes, and heterocyclic rings. In particular, we set up thirteen new aromaticity tests. We apply the tests to twelve aromaticity descriptors based on different physicochemical properties to identify their strengths and limitations depending on their accuracy in reflecting the expected aromaticity trends across the diverse types of organic molecules.

The tests proposed in this work are depicted in Scheme 1. The initial seven tests are focused on the lowest-lying triplet state (T_1) species. The following four involve the oxidation and/or reduction processes of molecules. In the final two tests, we compare the aromaticity in two heterocyclic isomeric molecules. The results obtained will demonstrate that common descriptors of aromaticity are not optimal to describe certain situations.

Measures of aromaticity

The twelve descriptors selected for this study are based on structural, magnetic, and electronic measures. Since we are expanding the previous work,[19] we selected the same indices that were chosen in that work, and we added the recently introduced electron density of delocalized bonds (EDDB) index.[32,33] It is worth noting that in a previous work,[34] EDDB was already applied to the tests of our initial fifteen tests.[19]

As a geometric-based measure, we have employed the harmonic oscillator model of aromaticity (HOMA) index, defined by Kruszewski and Krygowski.[35,36] It is the most widely used structural indicator of aromaticity, due to its straightforward computation and good performance considering its low computational cost. It can be obtained from the following expression:

$$HOMA = 1 - \frac{\alpha}{n}\sum_{i=1}^{n}(R_{opt} - R_i)^2 \qquad (1)$$

where n is the number of bonds that constitute the ring and the reference bond length, R_{opt}, is the optimal one for aromatic systems (1.388, 1.334, 1.265, and 1.309 Å for C–C, C–N, C–O, and N–N bonds, respectively). α is an empirical normalization factor (for C–C, C–N, C–O, and N–N bonds α = 257.7, 93.5, 157.4, and 130.3, respectively), determined by setting the HOMA value to 0 for a model non-aromatic system and HOMA = 1 for fully aromatic systems. As we can see in the expression, it only relies on geometrical data, R_i, which stands for a running bond length.

A new parametrization of this index for the excited states has been recently introduced, the HOMER, which stands for Harmonic Oscillator Model of Excited-state aRomaticity.[37] There is a key difference in the parameterization process. The R_{opt} is adjusted to bring both HOMA and HOMER values close to 1 for aromatic rings, however, α in this case, it is adjusted to yield HOMER values close to -1 for a model antiaromatic system. As a result, for non-aromatic systems, values are expected to fall near zero.

As magnetic indices of aromaticity, we have employed three variations of the nucleus-independent chemical shift (NICS) index; NICS(0), NICS(1), and NICS(1)$_{zz}$. This index was introduced by Schleyer and co-workers in 1996,[38] and it has been recognized as the most popular one, owing to the fact that it can also be obtained through experimental measures in some cases.[39] For example, NICS and NMR shifts of chemically inert ^{3}He at fullerene centers agree very well.[40] NICS is defined as the negative value of the absolute shielding computed at the ring center or at some other interesting point of the system. The aromatic character of the rings is reflected by negative NICS values, whereas positive NICS values indicate antiaromaticity.

Finally, seven aromaticity indicators based on the quantification of cyclic electron delocalization around the rings have been used.[27,41] These indices measure the cyclic electron delocalization of mobile electrons in aromatic rings. They use the delocalization index (DI)[42–44] between atoms A and B, $\delta(A,B)$, which is obtained by the double integration of the exchange-correlation
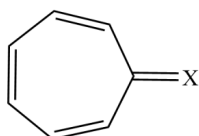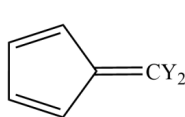
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Excited state aromaticity
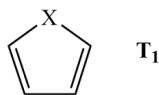
T16 - Heteroaromatic species (5-MRs)
X = CH$^-$, NH, O, CH$_2$, BH, CH$^+$
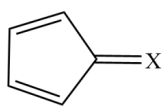
T17 - Pentafulvenes, I   T18 - Heptafulvenes, I
X = NH$_2^+$, O, NH, CH$_2$, BH$_2^-$

T19 - Pentafulvenes, II, S$_0$ T20 - Heptafulvenes, II, S$_0$
T21 - Pentafulvenes, II, T$_1$ T22 - Heptafulvenes, II, T$_1$
Y = NH$_2$, H, CN

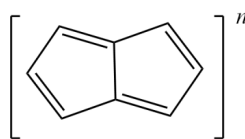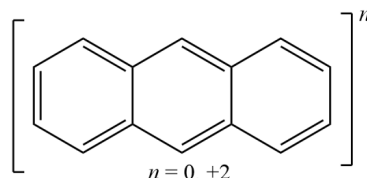**Aromaticity in redox processes**
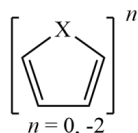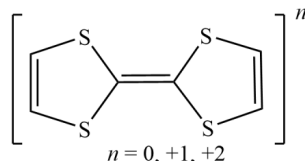
T23 - Borole
n = 0, -2

T24 - Tetrathiafulvalene
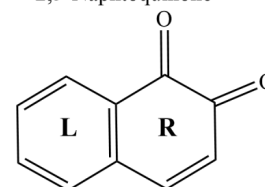n = 0, +1, +2

T25 - Pentalene
n = -2, 0, +2

T26 - Anthracene
n = 0, +2
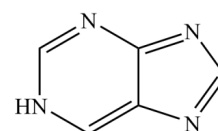
Isomeric polycyclic compounds
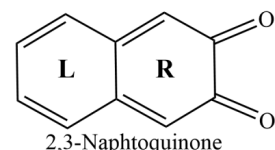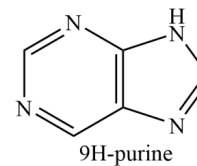
2,3-Naphtoquinone

1,2-Naphtoquinone

T27 - Quinones

1H-purine

9H-purine

T28 - Purines

Scheme 1 Schematic representation of the thirteen new proposed tests. Numbering starts at test T16 because in our previous work, we proposed fifteen tests (T1-T15).

density. For single-determinant closed-shell wavefunctions, the DI can be expressed in terms of atomic overlaps as:

$$\delta(A,B) = 2\sum_i \sum_j S_{ij}(A) S_{ij}(B) \qquad (2)$$

The summations in Eq. 2 run over all occupied molecular spin-orbitals. $S_{ij}(A)$ is the atomic overlap matrix of atom A, the overlap between molecular orbitals i and j integrated within the basin of atom A. This integration in the present work has been carried out in the framework of the quantum theory of atoms-in-molecules (QTAIM).[43,45]

As electronic-based indices, first, we have employed the *para*-delocalization index (PDI),[46,47] which is computed by averaging the DI's between atoms located in *para*-positions within the six-membered rings (6-MRs). It was inspired by the fact that benzene exhibits greater electron sharing between carbons in *para*- than in *meta*-positions.[48,49] Therefore, the higher the value, the more aromatic the molecule is expected to be.

Second, we have the aromatic fluctuation index (FLU) by Matito *et al.* defined in 2005.[50,51] It measures aromaticity by assessing the uniformity of cyclic electron delocalization along the

ring and comparing it to that of well-known aromatic molecules.

$$FLU(\mathscr{A}) = \frac{1}{N}\sum_{i=1}^{N}\left[\left(\frac{V(A_i)}{V(A_{i-1})}\right)^{\alpha}\left(\frac{\delta(A_i,A_{i-1}) - \delta_{ref}(A_i,A_{i-1})}{\delta_{ref}(A_i,A_{i-1})}\right)\right]^2 \qquad (3)$$

Here $A_0 \equiv A_N$ and $V(A)$ is the atomic valence of atom A as defined by Eq. 4 for a closed-shell system:

$$V(A) = \sum_{A\neq B}\delta(A,B) \qquad (4)$$

and α is a simple function, Eq. 5, which ensures that the ratio of adjacent atomic valences always takes values greater than or equal to one:

$$\alpha = \begin{cases} 1 & \text{for} \quad V(A_i) > V(A_{i-1}) \\ -1 & \text{for} \quad V(A_i) \geq V(A_{I-1}) \end{cases} \qquad (5)$$

Finally, the $\delta_{ref}(A_i, A_{i-1})$ values are $\delta_{ref}(C,C) = 1.389$e, $\delta_{ref}(C,N) = 1.318$e, $\delta_{ref}(N,N) = 1.518$e, and $\delta_{ref}(C,O) = 0.970$e taken from benzene, pyridine, pyridazine, and furan, respectively, at the B3LYP/6-311++G(d,p) level. Aromatic molecules present FLU values close to zero, and the value increases as the aromaticity of the ring decreases. The original FLU index, designed for closed-shell systems, was adapted for Baird aromaticity analysis by splitting it into α and β components.[52] We will employ FLU$^{1/2}$

instead of FLU, since although both follow analogous trends, a key advantage of $FLU^{1/2}$ is that it displays a wider range, thereby offering clearer trends.[53]

Third, we have employed a set of four multicenter indices, namely, the I_{ring}, I_{NG}, MCI, and I_{NB}. The multicenter index (I_{ring}) of Giambiagi et al. studies the electron delocalization around the ring by applying the following Eq. 6 for a closed-shell monodeterminantal wavefunction:[54]

$$I_{ring}(\mathscr{A}) = 2^N \sum_{i_1,i_2,...,i_N}^{occ.MO} S_{i_1,i_2}(A_1)S_{i_2,i_3}(A_2)...S_{i_N,i_1}(A_N) \qquad (6)$$

Considering that the electron sharing is not constrained to neighbouring atoms, Bultinck et al. proposed an extension of the I_{ring} named the multicenter electron delocalization index (MCI), whose formula reads:[55]

$$MCI(\mathscr{A}) = \frac{1}{2N} \sum_{P(\mathscr{A})} I_{ring}(\mathscr{A}) \qquad (7)$$

where $P(\mathscr{A})$ stands for a permutation operator to generate the $N!$ permutations of the elements in string $\mathscr{A}$, to ensure that all contributions from every possible rearrangement of the atoms of the ring are taken into account. Generally, when working with organic molecules, these two indices demonstrate a significant correlation since the major contribution to MCI comes from the Kekulé structure. The more aromatic the rings are, the higher the I_{ring} and MCI are.

These indices are ring-size dependent; therefore, to enable the comparison between rings of different sizes, normalized versions have been introduced. A proposed normalized version of the I_{ring} index is the so-called I_{NG}, which is expressed as:[56]

$$I_{NG}(\mathscr{A}) = \frac{\pi^2}{4Nn_\pi} I_{ring}^{1/N} \qquad (8)$$

where N is the total number of atoms in the ring and n_π the total number of π-electrons. A normalized version of the MCI index is the I_{NB}, and it is given by Eq. (9), where $C \approx 1.5155$.[56]

$$I_{NB}(\mathscr{A}) = \frac{C}{Nn_\pi}[2NMCI(\mathscr{A})]^{1/N} \qquad (9)$$

To apply these indices to the lowest-lying triplet excited states (T_1), the same strategy used for the FLU index is followed, performing the calculations separately for the α and β components.[57]

The last electronic index is the electron density of delocalized bonds (EDDB),[32–34] which quantifies the electron delocalization throughout the system. It is an electron density (ED) partitioning method, where the ED is divided into several "layers" corresponding to different levels of electron delocalization,[58] which are the electron density localized on atoms (EDLA), the electron density of localized bonds (EDLB), and the EDDB, which accounts for the remaining density that cannot be assigned to specific atoms or bonds due to its multicenter delocalized nature. EDDB offers predictions closely aligned with MCI but at much lower computational cost, enhancing efficiency, particularly for large molecules and correlated wavefunctions.

For the purpose of this work, we have evaluated the number of cyclically delocalized electrons in a given path (usually the path that follows the perimeter of the ring studied, $EDDB_P$). This function does not account for cross-ring delocalization effects; it is restricted to the delocalization arising from the resonance of the Kekulé forms. Moreover, the $EDDB_P$ values have been normalized by dividing them by the number of atoms in the path to express the number of delocalized electrons per atom. Aromatic molecules with a high degree of delocalization yield higher values.

Computational details

Geometry optimizations have been performed using Gaussian 16[59] at the B3LYP[60,61] level of theory with the 6-311++G(d,p) basis set.[62] For closed-shell ground state species, geometry optimizations and calculations of aromaticity indices have been carried out using the restricted formalism at the B3LYP/6-311++G(d,p) level of theory. In contrast, open-shell triplet states have been treated with the unrestricted formalism for both geometry optimization and the evaluation of aromaticity descriptors (UB3LYP/6-311++G(d,p)). For comparison purposes, we have kept the same level of theory as in our previous studies,[19,63] although we are aware of the superior performance of long-range corrected functionals in aromatic species.[64–67] However, we do not expect significant changes in aromaticity trends by changing the functional or the basis set.[66,67] The numerical accuracy of the QTAIM calculations done with the AIMPAC program[68] has been assessed using two criteria: (i) The integration of the Laplacian of the electron density ($\nabla^2 \rho(r)$) within an atomic basin should be close to zero; (ii) the total number of electrons in a molecule must equal the sum of all the electron populations within the molecule and also match the sum of all localization indices plus half of the delocalization indices. For all atomic calculations, integrated absolute values of $\nabla^2 \rho(r)$ were consistently below 0.001 a.u. For all molecules, the error in the calculated number of electrons was always less than 0.01 a.u.

Calculations of electronic and structural descriptors of aromaticity were performed with the ESI-3D program,[69] except for $EDDB_P$ and HOMER. The $EDDB_P$[32–34] indices were obtained using the NBO 7.0 software[70] to first derive the natural atomic orbitals (NAO)[71] and the one-electron density matrix required by the RunEDDB program.[72] The excited-state analogue of HOMA, known as HOMER,[37] was computed using the ESIpy program.[73] The GIAO method[74] has been used for the calculations of NICS[38] at the ring center (NICS(0)), determined by the non-weighted mean of the heavy atom coordinates, and at 1 Å above and below the ring plane, NICS(1) and NICS(-1). We have also analysed its out-of-plane component, $NICS(1)_{zz}$.[75] All these indicators of aromaticity have been computed for both closed-shell ground state species and open-shell triplet excited states.

Results and Discussion

1. Triplet State Aromaticity - Baird's $4n$ Rule

1.1. Five-Membered Rings

Test T16 is an extension of test T11, previously described in the article by Feixas *et al.*,[19] to the lowest-lying triplet excited state, T_1. It involves a series of six heteroaromatic 5-MRs, in which the degree of aromaticity depends on the electron-donating character of the heterogroup X within the ring. The greater the electron-withdrawing character of the X group, the larger the aromaticity of the ring since it will approach the 4π-electrons required to fulfil $4n$ Baird's rule.[76] Consequently, the expected order of aromaticity is $CH^+ > BH > CH_2 > O > NH > CH^-$, just the contrary of that of the T11 test.

With the exception of NICS(1) and NICS(1)$_{zz}$, which correctly order the six species and correctly categorize them, the rest of the indices fail to some extent (see Table S19). The descriptors show inferior performance in the T_1 state than in the S_0 ground state, as several electronic indices had previously provided correct trends in the S_0 state (see T11 in Table 1 and Table S12) but not in the T_1 state. However, if we look closely at the results, we can see that MCI and I_{NB} only fail to assign a certain aromatic character to the most antiaromatic species ($R = CH^-$). The other multicenter indices, I_{ring} and I_{NG}, also fail by attributing similar values to the species with $R = -O$ and $-CH_2$, whereas EDDB$_P$ assigns a similar value to the species with R=-NH as well. FLU$^{1/2}$, HOMA, and HOMER do not work well either. We attribute the failure of the FLU$^{1/2}$ and HOMA to the fact that they were parameterized for the ground state.

1.2 Fulvenes I

Tests T17 and T18 constitute a series designed to explore the influence of exocyclic substituents with different electrodonating character on the aromatic character of fulvene molecules. Again, these molecules have already been studied in the previous work in their singlet ground state (S_0),[19] and we now extend the analysis to examine the capability of the descriptors to reflect the aromaticity changes in their lowest-lying triplet excited state (T_1). Accordingly, the anticipated trends will be based on Baird's rule.[76,77]
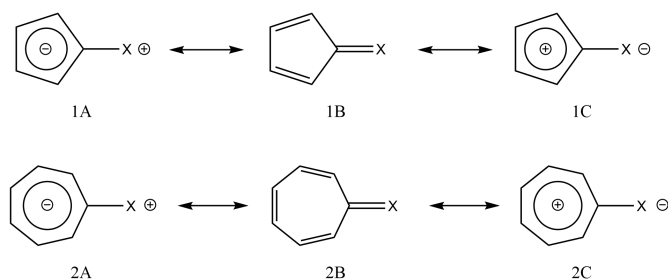

Fig. 1 The most relevant resonance structures of fulvenes I ($X = NH_2^+$, O, NH, CH_2, BH_2^-) and fulvenes II ($X = CY_2$, Y = NH_2, H, CN).

The impact of the electron-donating and electron-withdrawing character of the substituents can be comprehended by the varying contributions of the resonance structures in Fig. 1.[78–80] In the presence of electron-withdrawing groups (EWGs), which pull electron density away from the ring, the structures 1C and 2C are stabilized with 4 and 6π-electrons within the ring, respectively. Hence, the aromatic character of the 5-MR in pentafulvenes, taking into account Baird's $4n$ aromaticity rule, is predicted to increase following the trend: $NH_2^+ > O > NH > CH_2 > BH_2^-$. Conversely, electron-donating groups (EDGs) enhance the aromaticity in the heptafulvenes in their T_1 by stabilizing structure 2A, leaving the 7-MR with 8π-electrons, thus resulting in the opposite trend. To assess the influence of substituents on aromaticity, molecular geometries were optimized imposing a planar conformation. This ensures that the p_z orbitals of the substituents are oriented perpendicular to the molecular plane, allowing optimal interaction between these p_z orbitals and those of the ring.

In the preceding ground-state analysis,[19] only MCI, I_{NB}, and the NICS variants reproduced the exact aromaticity order across both sets of species (see T13 in Table 1 and Table S14). In the T_1 state, HOMER, together with the aforementioned indices, accurately captures the trends for the pentafulvenes (see Table S20). HOMA, I_{ring}, and I_{NG} fail to properly rank cyclopentadienone and assign similar aromatic characters to the mid-range species. EDDB$_P$ fails in the ordering of just R = BH_2^- and FLU$^{1/2}$ struggles with the overall ordering. For the heptafulvenes, most indices generally perform well. The exceptions are HOMA and FLU$^{1/2}$, which both fail switching R = NH_2^+ and R = O. Moreover, these two species have the same I_{NG} value. The quantifiers that rank the molecules correctly are HOMER, NICS, and the rest of the electronic indices, with all indices consistently indicating low aromaticity overall.

1.3 Fulvenes II

These four tests, labelled T19 through T22, further evaluate the ability of the quantifiers to describe changes in aromatic character according to the electron-donating character of the substituents, which are now placed in an exocyclic carbon atom ($X = CY_2$, Y = NH_2, H, CN), of fulvenes in their S_0 and T_1 states. The expected trends can be explained by the weight of the resonance structures in Fig. 1. As in the previous tests, molecular geometries were optimized with a constrained planar conformation to ensure overlap between p_z orbitals of the substituents and the ring.

Considering the increased contribution of resonance structure 1A with formally 6π-electrons in the presence of an EDG, an increase in the aromaticity is expected in the S_0 state of pentafulvenes following the order $NH_2 > H > CN$. In contrast, the aromatic character of the 7-MRs in heptafulvenes decreases in the same order because of the large contribution of the 8π-electron structure 2A. In the T_1 state, in which Baird's rule applies,[76] EDGs enhance the aromatic character in heptafulvenes in the same order $NH_2 > H > CN$, as the system fulfils the $4n$ rule, and decrease it in pentafulvenes. On the other hand, stabilizing structures 1C and 2C, EWGs are expected to lead to the converse situation, increasing the aromatic character for heptafulvenes in their ground state in the order $CN > H > NH_2$, due to an increase in the resonance structure with 6π-electrons within the ring, and dropping in the 5-MRs with 4π-electrons in pentafulvenes in the same order. In the T_1 state, the EWGs strengthen the aromatic character

in pentafulvenes and reduce it in heptafulvenes.[78,81–83] Thus, a good aromaticity descriptor should give the following order of aromaticity for the 5-MRs in pentafulvenes in their S_0 state NH_2 > H > CN, and the same is expected for the heptafulvenes in their triplet excited state. For the 7-MR in heptafulvenes in their S_0 state and the pentafulvenes in their T_1 state, the opposite order is anticipated.

The complete set of indicators provides the expected trends (see Table S21) for both the S_0 and T_1 states of penta- and heptafulvenes, with the exception of I_{ring} and I_{NG} that provide similar aromaticities to Y = H and CN in T22.

2. Redox Species

2.1 Borole

In test T23, we evaluate the efficiency of the descriptors in reflecting the increase in aromaticity of the borole, a 4π-electron antiaromatic molecule,[84–88] after gaining two π-electrons, hence, meeting the Hückel's $4n + 2$ aromaticity rule for ground state molecules.[89]

All indices indicate an increase in aromaticity following reduction (see Table S22). Nevertheless, the aromaticity descriptors suggest that the aromatic character of the dianionic species remains very weak and the actual values of the indices are so low that the molecule could reasonably be classified as non-aromatic or at least weakly aromatic, as found in previous studies.[85]

2.2 Tetrathiafulvalene (TTF)

In test T24, the quantifiers are evaluated over the enhancement in aromaticity through the oxidation of the TTF, a non-aromatic compound.[90,91] According to the empirical electron counting rules, the neutral species has 7π-electrons per ring. The two rings are not exactly in the same plane showing a boat-like structure with C_{2v} symmetry.[92] Upon oxidation, a π-electron is lost, and one ring is left with 6π-electrons, thereby satisfying the $4n + 2$ rule. As a matter of fact, this gained aromatic character is spread between the two rings that are now in the same plane, with the radical cation having D_{2h} symmetry.[93] This behaviour can be explained by the resonance between the two structures illustrated in Fig. 2. Moreover, as we can visualize, the bond between the two rings now has a partial double bond character with only one π-electron.
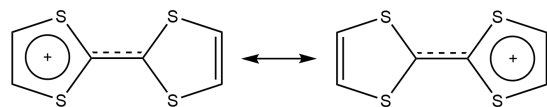

Fig. 2 Resonance structures of the cationic TTF$^{+\cdot}$.

Finally, after removing another electron and reaching the $+2$ charge, the two rings end up with 6π-electrons each, which further enhances the aromatic character, becoming fully aromatic. Furthermore, the bond has completely lost its double-bond character, allowing free rotation of the rings and resulting in a loss of planarity in the overall conformation.[94]

The entire set of indices effectively describes the aromatic trend (see Table S23). Moreover, almost all the indices correctly describe the non-aromatic character of the neutral species by giving values close to zero, with the exception of NICS(0), that classifies the rings of the neutral species as aromatic.

2.3 Pentalene

Test T25 assesses the ability of the twelve indices to describe the change in the aromaticity of pentalene as its charge varies, leading to changes in the number of π-electrons. In its neutral state, it presents 8π-electrons, 4 in each ring, which satisfies the $4n$ Hückel rule for antiaromatic species.[86,95] These fused conjugated rings can potentially acquire aromaticity through oxidation or reduction. These increases in aromaticity can be explained in two ways: from a global point of view, where the resulting ions are expected to behave as peripherical aromatic systems with 6 or 10 π-electrons,[96] or from a local point of view, where one of the rings becomes compliant with the $4n + 2$ rule, with either 2 or 6 π-electrons, and due to resonance, as illustrated in Fig. 3, both rings acquire partial aromatic character.
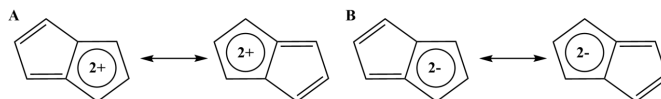

Fig. 3 Resonance structures of A) the dicationic and B) the dianionic pentalene.

All indices in the set were suitable for describing the increase in aromaticity following the reduction. However, the increase in aromaticity upon formation of the dicationic species was not consistently captured by the entire collection of quantifiers (see Table S24). The four multicenter indices, I_{ring}, I_{NG}, MCI, and I_{NB} fail to show the increase in aromaticity after oxidation. This can be attributed to the fact that these quantifiers assess the extent of electron delocalization within the ring. Upon oxidation, the removal of electrons reduces the number of electrons available for delocalization, thereby decreasing the values and diminishing the effectiveness of these electronic indices. Interestingly, although the EDDB$_P$ analysis indicates an increase in aromaticity in both directions, the change observed after oxidation is comparatively smaller, which could be argued in a similar manner. Furthermore, HOMA also fails to reflect this increase. Moreover, NICS gives positive values for the aromatic dianion. Given all that, the descriptors that described the expected trend in T25 are FLU$^{1/2}$, EDDB$_P$, and NICS.

2.4 Anthracene

T26 analyses anthracene and doubly oxidized anthracene. Considering Clar's rule,[97,98] anthracene presents a migrating π-sextet, therefore, all three rings should exhibit similar aromatic character and this is what most indices show.[99] After the oxidation of the system down to 12π-electrons, according to Clar's rule, the dication features two π-sextets localized in the external rings (Fig. 4).[100,101] Consequently, the indices should reflect an increase in aromaticity in the outer rings, accompanied by a decrease in the inner ring, which formally loses all its π-electrons and becomes non-aromatic or at least less aromatic than the external ones.
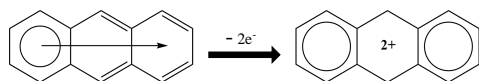
Fig. 4 Clar's structure of the neutral and dicationic anthracene.

Analysing each species separately, in general, the indices successfully capture the similar aromatic character of the external rings expected in both, the neutral and the dicationic, as well as the resemblance between the external and internal rings in the neutral molecule. The decrease in the aromaticity of the central ring after oxidation was consistently reflected by all indices. Conversely, an increase in the outer rings is indicated only by I_{ring}, $FLU^{1/2}$, HOMA, and $EDDB_P$ indices. Yet most of these indices underestimate the expected variations, as the reported changes are often smaller than the differences observed between rings within the neutral species, where no significant variance is expected. Taking all of the above into account, the only index that aligns with all expected trends in test T26 is $FLU^{1/2}$ (see Table S25).

3. Isomeric Molecules
3.1 Quinones

This test, T27, studies the changes in aromaticity between two naphtoquinones (see Scheme 1). The presence of the two keto groups at different positions leads to a different rearrangement of the four remaining double bonds, which raises different aromatic characters[102,103]. Larger aromaticity is expected in the left/unsubstituted ring of the most stable 1,2-naphthoquinone[103] (quinone B, $Q_B - L$) due to the formation of the π-sextet, whereas the left/unsubstituted ring of 2,3-naphtoquinone (quinone A, $Q_A - L$) is expected to be weakly aromatic due to the existence of its zwitterionic structure illustrated in Fig. 5. Meanwhile, weak or no aromaticity is predicted in the right rings ($Q_A - R$ and $Q_B - R$). Therefore, the expected order of aromaticity is: $Q_B - L \gg Q_A - L \gtrsim Q_A - R \approx Q_B - R$.
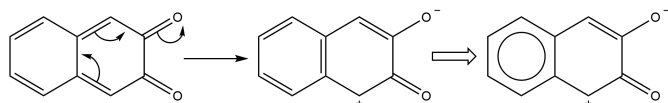

Fig. 5 The zwitterionic structure of 2,3-naphtoquinone.

The complete set of indices captures the decrease between left-side rings, from the highly aromatic $Q_B - L$ to the slightly aromatic $Q_A - L$. Still, some indices exhibit limitations (see Table S26). NICS correctly classifies $Q_B - L$ as aromatic but misclassifies the rest, assigning values shifted toward the antiaromatic region, despite these being expected to be slightly aromatic or non-aromatic. A similar issue is observed with the HOMA index, which indicates non-aromaticity for $Q_A - L$ and antiaromaticity for $Q_{A/B} - R$. Interestingly, this geometric index is the only one that displays a larger difference between $Q_A - L \gtrsim Q_A - R$ than between $Q_B - L \gg Q_A - L$, which is inconsistent with the expected aromaticity trend. In contrast, $FLU^{1/2}$ values increase in line with expectations, making it a reliable quantifier alongside the multicenter indices, which also offer an accurate description.

3.2 Purine

Test T28 studies the difference in aromaticity between two isomeric purines (see Scheme 1) that differ in the position of the NH unit, from which the π-electron pair in the $2p_z$ orbital of the nitrogen atom is available to be delocalized along the π-system of the ring.[104] Therefore, when the NH unit is present in the 5-MR, as in the 9H-tautomer, the two rings contain 6π-electrons, *ergo*, both of them follow the $4n + 2$ Hückel's rule.[89] On the other hand, the 1H-tautomer has a 5-MR with 5π-electrons and a 6-MR with 7π-electrons, resulting in a significantly lower aromaticity.[105]

The increase in aromaticity from 1H-purine to the 9H-purine between the two 6-MRs is correctly captured by all quantifiers (see Table S27). On the contrary, only NICS(0), $EDDB_P$, and HOMA indicate an increase when going from the 5-MR of 1H-purine to 9H-purine. Moreover, this geometric, computationally inexpensive index also provides a good qualitative description of the aromatic character, yielding values close to 1 for the aromatic rings in 9H-purine, and lower values that still fall within the aromatic range (between 0 and 1) for the two rings in 1H-purine.

Conclusions

As a concluding set of recommendations derived from the analysis of the thirteen tests applied to the twelve aromaticity indices studied, we can say that, first, in general, indicators of aromaticity perform somewhat better in the S_0 than in the T_1 state; second, NICS and $EDDB_P$ are the quantifiers with the highest reliability in these new introduced tests (T16-28), although caution should be exercised when using these magnetic indices in fused rings;[21,106,107] third, multicenter indices, which have long been regarded as the most reliable ones, have presented a consistent tendency to encounter difficulties when working on oxidized species; fourth, for the T_1 state, HOMER overperforms HOMA, although application of HOMER to fused systems (for instance, biphenylene) remains to be explored; fifth, $EDDB_P$ performs as good as MCI but at much lower computational cost. Finally, since no index performs reliably in all cases, we continue to recommend using a set of indices based on different properties to reach more reliable conclusions.

Table 1 Summary of the results of the twenty-eight tests applied at the B3LYP/6-311++G(d,p) level for the twelve descriptors of aromaticity analysed. Tests T16-T28 are the new proposed tests."Yes," "No," "N/A," and "Unclear" mean that the index passes the test, it does not pass the test, the test is not applicable for this index, and the test fails only in the ordering of one molecule, respectively.

	PDI[a]	FLU$^{1/2}$	MCI	I_{NB}	I_{ring}	I_{NG}	EDDB$_P$	HOMA	HOMER[b]	NICS(0)	NICS(1)	NICS(1)$_{zz}$
T1	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Unclear[c]	N/A	Yes	Yes	Yes
T2	Unclear[d]	Yes	Yes	Yes	Yes	Yes	Yes	Unclear[c]	N/A	Unclear[e]	Yes	Yes
T3	Unclear[d]	Yes	Yes	Yes	Yes	Yes	Yes	Yes	N/A	Yes	Yes	Yes
T4	Unclear[d]	Yes	Yes	Yes	Yes	Yes	Yes	Yes	N/A	Yes	Yes	Yes
T5	Unclear[d]	Yes	Yes	Yes	Yes	Yes	Yes	Yes	N/A	Yes	Yes	Yes
T6	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Unclear[f]	N/A	No	No	Yes
T7	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	N/A	No	No	Yes
T8	N/A	Yes	Yes	Yes	Yes	Yes	Yes	Yes	N/A	No	Yes	Yes
T9	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	N/A	Yes	No	No
T10	No	Unclear[g]	Unclear[h]	Unclear[h]	Unclear[h]	Unclear[h]	No	No	N/A	No	No	No
T11	N/A	Unclear[g]	Yes	Yes	Yes	Unclear[g]	Unclear[g]	Unclear[g]	N/A	Unclear[g]	Unclear[g]	Yes
T12	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	N/A	Yes	Yes	Yes
T13	N/A	No	Yes	Yes	Unclear[g]	Unclear[g]	Unclear[g]	Unclear[g]	N/A	Yes	Yes	Yes
T14	Yes	No	Yes	Yes	Yes	Yes	Yes	No	N/A	Unclear[i]	Unclear[i]	Yes
T15	Yes	No	Yes	Yes	Yes	Yes	Yes	No	N/A	Unclear[i]	Unclear[i]	Unclear[i]
T16	N/A	No	Unclear[g]	Unclear[g]	Unclear[g,j]	Unclear[g,j]	Unclear[g,j]	No	No	Unclear[g]	Yes	Yes
T17	N/A	No	Yes	Yes	Unclear[g]	Unclear[g]	Unclear[g]	Unclear[g]	Yes	Yes	Yes	Yes
T18	N/A	Unclear[g]	Yes	Yes	Yes	Yes	Yes	Unclear[g]	Yes	Yes	Yes	Yes
T19	N/A	Yes	Yes	Yes	Yes	Yes	Yes	Yes	N/A	Yes	Yes	Yes
T20	N/A	Yes	Yes	Yes	Yes	Yes	Yes	Yes	N/A	Yes	Yes	Yes
T21	N/A	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
T22	N/A	Yes	Yes	Yes	Unclear[g]	Unclear[g]	Yes	Yes	Yes	Yes	Yes	Yes
T23	N/A	N/A	Yes	Yes	Yes	Yes	Yes	Yes	N/A	Yes	Yes	Yes
T24	N/A	Yes	Yes	Yes	Yes	Yes	Yes	Yes	N/A	Yes[k]	Yes	Yes
T25	N/A	Yes	No	No	No	No	Yes	No	N/A	Yes[k]	Yes[k]	Yes[k]
T26	Unclear[g]	Yes	Unclear[g]	Unclear[g]	Unclear[g]	Unclear[g]	Yes	Yes	N/A	No	No	No
T27	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Unclear[k,l]	N/A	Unclear[k]	Unclear[k]	Unclear[k]
T28	Yes	No	No	Unclear[j]	No	No	Yes	Yes	N/A	Yes	No	No

[a]Only applicable to 6-MR's.
[b]Only applied to molecules in their T_1 state.
[c]Loss of aromaticity is overemphasized (see ref. [19]).
[d]The aromaticity remains almost unchanged with the distortion (see ref. [19]).
[e]The trend in aromaticity remains almost unchanged with some oscillations (see ref. [19]).
[f]The aromaticity is higher than that of benzene only for a small number of molecules (see ref. [19]).
[g]Fails only in ordering one molecule (see ref. [19]).
[h]Fails only in ordering one molecule (see text). At the CCSD level, this index passes the test.
[i]The aromaticity of the TS is higher than that of benzene (see ref. [19]).
[j]Fails only by assigning nearly identical character to two molecules (see text).
[k]Trend is correct but the classification of some of the species as (anti)aromatic is wrong (see text).
[l]The proportions are not right (see text).

Author contributions

M.S.: conceived the project, acquired funding, provided resources, supervised the project, and wrote, reviewed, and edited the manuscript.

M.C.: Performed DFT calculations, analyzed the data, and wrote, reviewed, and edited the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/xxxxxxx

Acknowledgements

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DATA AVAILABILITY STATEMENT

The data supporting this article have been included as part of the supplementary information (SI).