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1 Article

2 Are multicentre bond indices and related quantities 3 reliable predictors of excited-state aromaticity?

4

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13 **Abstract:** Systematic scrutiny is carried out of the ability of multicentre bond indices and the NOEL-
14 based similarity index d_{AB} to serve as excited-state aromaticity criteria. These indices were calculated
15 using state-optimized complete active-space self-consistent field wavefunctions for several low-
16 lying singlet and triplet states of the paradigmatic molecules of benzene and cyclobutadiene and the
17 inorganic ring S_2N_2 . The comparison of the excited-state indices with aromaticity trends for
18 individual excited states suggested by the values of magnetic aromaticity criteria show that whereas
19 the indices work well for aromaticity reversals between the ground singlet and first triplet electronic
20 states, addressed by Baird's rule, there are no straightforward parallels between the two sets of data
21 for singlet excited states. The problems experienced while applying multicentre bond indices and
22 d_{AB} to singlet excited states are explained by the loss of the information inherently present in
23 wavefunctions and/or pair densities when calculating the first-order density matrix.

24 **Keywords:** excited-state aromaticity reversals, multicentre bond indices, molecular similarity,
25 magnetic properties of excited states

26

27 1. Introduction

28 Despite its somewhat vaguely defined qualitative nature, the concept of aromaticity has had
29 huge impacts on organic chemistry, starting with the formulation of the Hückel aromaticity rules [1,
30 2] and encompassing a broad research area including the elucidation of the link between cyclic
31 delocalization and energetic stabilization of conjugated (poly)cyclic hydrocarbons [3–10], the role of
32 cyclic conjugation in inducing the ring currents [11–19] responsible for the special magnetic
33 properties of aromatic compounds, and revealing the links between electron counts, orbital topology
34 and selection rules in pericyclic reactions [20–23]. The fact that the phenomenon of aromaticity can
35 be associated with a very wide range of structural, energetic, and magnetic properties [3–14, 16–18,
36 24, 25] has given impetus to numerous attempts to define measures or indices that are intended to
37 characterize the “extent” of aromaticity in quantitative terms [16–19, 24–33]. However, such efforts
38 have often been plagued by discrepancies between the various types of indices; these have led to the
39 postulation of a multidimensional character for this phenomenon [34–36], even implying
40 “orthogonality” between energetic and magnetic measures of aromaticity as manifested by the
41 reported absence of a straightforward link between these two types of aromaticity measure [19, 29,
42 37, 39]. However, it has been demonstrated that such discrepancies are most often observed when
43 trying to juxtapose quantities that are not straightforward to compare. One such example is provided

44 by attempts to correlate the extents of cyclic delocalization in the individual benzene rings in
45 polycyclic aromatic hydrocarbons (PAHs), as given by multicentre bond indices, with the values of
46 nucleus-independent chemical shieldings (NICS) [18]. This fails not least because of the
47 incompatibility between the strictly local character of multicentre indices and the fact that the NICS
48 value for an individual ring is “contaminated” by the interfering contributions of the other rings
49 [37,39]. The agreement between these two types of index is in fact restored when the contaminating
50 contributions are properly taken into account; analogous parallels have been established between
51 multicentre indices, induced ring currents and (when properly accounted for) the energetic effects of
52 cyclic conjugation [19, 37–41].

53 Although initially most studies were focused on aromaticity in ground electronic states, Baird’s
54 pioneering discovery of the reversal of Hückel’s aromaticity rules upon electronic excitation from the
55 singlet ground to the first triplet excited state [42] directed attention to the systematic investigation
56 of excited-state aromaticity [43–51]. The importance of such studies for the understanding of the
57 photochemical/physical properties of photoactive materials has prompted the development of
58 experimental and computational tools that are capable of providing reliable estimates of excited-state
59 aromaticity. Amongst the first attempts at theoretical justification of Baird’s discovery of aromaticity
60 reversals in the lowest excited states of cyclic conjugated hydrocarbons is a study by Ilić *et al.* [43]
61 which looked at the extension of the concept of topological resonance energy (TRE) to low-lying states
62 of cyclic conjugated hydrocarbons. The authors of that study demonstrated that the TRE values for
63 the ground and lowest excited states of conjugated rings reproduce the aromaticity reversal predicted
64 by Baird’s rule. Despite the elegant simplicity of this approach, the calculation of TREs has serious
65 inherent limitations arising from the Hückel molecular orbital (HMO) foundations of the underlying
66 graph-theoretical considerations. Modern quantum chemical calculations are not subject to such
67 limitations and the scope of excited-state aromaticity studies was subsequently extended to
68 formulating Baird-style rules for higher excited states. The most convincing proof of aromaticity
69 and/or antiaromaticity reversals in the first and higher excited states was provided by the results of
70 systematic studies of various magnetic properties with state-specific complete active-space self-
71 consistent field (CASSCF) wavefunctions constructed from gauge-included atomic orbitals (GIAOs)
72 [44–46, 52]. Given that multicentre bond indices have been applied successfully for the quantitative
73 evaluation of the local aromaticities of individual benzene rings in PAHs [28, 29, 37, 40], it was natural
74 to try to find out whether the same approach could provide a computationally efficient and
75 sufficiently accurate characterization of excited-state aromaticity. The aim of the current work is to
76 carry out a systematic comparative study of the performance and reliability of multicentre bond
77 indices and other first-order density-based quantities for the description and classification of excited-
78 state aromaticity in the paradigmatic molecules benzene and cyclobutadiene, as well as in disulfur
79 dinitride, which has been shown recently to be the first inorganic ring that exhibits changes in
80 aromaticity between different electronic states [52]. As will be shown, it turns out that such quantities
81 have significant difficulties distinguishing properly between singlet diradical and zwitterionic
82 character.

83 2. Computational methodology

84 2.1 Electronic structure calculations

85 The aromaticity of the low-lying electronic states of benzene, square cyclobutadiene and disulfur
86 dinitride has been analysed using a range of magnetic criteria including NICS calculated with
87 CASSCF-GIAO wavefunctions at fixed ground electronic state geometries [27, 44–46, 52]. To enable
88 direct comparisons, we use the same levels of theory and the same geometries in the current work.
89 All excited electronic state properties discussed in this work correspond to vertical excitations
90 because we chose to use identical ground-state geometries for all electronic states of a given molecule.
91 All CASSCF calculations on benzene and cyclobutadiene reported in this paper were carried out
92 within the 6-311++G(2d,2p) basis, whereas use was made of the cc-pVTZ basis for S₂N₂.

93 It is important in this work to focus on vertical excitations not least because the electronic
94 wavefunction changes much more rapidly than the molecular geometry. By examining the excited-

95 state wavefunction at the ground-state geometry we can establish whether a given vertically excited
 96 state is intrinsically aromatic, antiaromatic or non-aromatic. If it turns out to be aromatic then it will
 97 of course tend to retain a geometry that is similar to that of the ground state. If, on the other hand, it
 98 is antiaromatic then it is likely to experience a geometry distortion that leads to a lower-energy, less
 99 antiaromatic and closer to non-aromatic geometry. The same does of course apply for systems which
 100 are antiaromatic in their electronic ground states, such as the ground state of square (D_{4h})
 101 cyclobutadiene; the relaxation of the geometry of that system to rectangular (D_{2h}) decreases the
 102 antiaromaticity, not only making this state much more non-aromatic but also rendering it
 103 significantly less interesting to study as an example of an antiaromatic molecule.

104 The S_0 (1^1A_{1g}), T_1 (1^3B_{1u}), S_1 (1^1B_{2u}) and S_2 (1^1B_{1u}) electronic states of benzene were described
 105 using state-optimized π -space CASSCF(6,6) wavefunctions (with “6 electrons in 6 orbitals”). We used
 106 the experimental D_{6h} gas-phase ground-state geometry with C–C and C–H bond lengths of 1.3964 Å
 107 and 1.0831 Å, respectively, which was obtained through analysis of the ν_4 vibration-rotation bands of
 108 C_6H_6 and C_6D_6 [53].

109 The calculations for the S_0 (1^1B_{1g}), T_1 (1^3A_{2g}), S_1 (1^1A_{1g}) and S_2 (1^1B_{2g}) electronic states of square
 110 (D_{4h}) cyclobutadiene employed state-optimized π -space CASSCF(4,4) wavefunctions (with “4
 111 electrons in 4 orbitals”). We used C–C and C–H bond lengths of 1.447 Å and 1.076 Å, respectively,
 112 that were optimized with the cc-pVTZ basis through a multireference averaged quadratic coupled
 113 cluster (MR-AQCC) approach, taking orbitals from corresponding state-averaged π -space
 114 CASSCF(4,4) wavefunctions that included the ground state, lowest triplet state and two lowest singlet
 115 excited states (SA-4-CASSCF) [54].

116 The calculations on the S_0 (1^1A_g), T_1 (1^3B_{3u}) and S_1 (1^1A_u) electronic states of S_2N_2 were carried
 117 out using state-optimized CASSCF(22,16) wavefunctions (with “22 electrons in 16 orbitals”). For this
 118 purpose we used the D_{2h} semi-experimental equilibrium geometry established by Perrin *et al.* [55],
 119 with $R(SN) = 1.64182$ Å and $\angle(NSN) = 91.0716^\circ$, in a coordinate system that places N at positions
 120 (± 1.171748 Å, 0.0, 0.0), and S atoms at positions (0.0, ± 1.150035 Å, 0.0), respectively.

121 All of the CASSCF calculations required for the present work were primarily carried out using
 122 Gaussian 03 [56] but, purely for our convenience, the same wavefunctions were also obtained using
 123 MOLPRO [57, 58]. For reasons that we have explained, it was important to use the ground-state
 124 geometries for all of these calculations. We note in passing that accurate excited-state geometry
 125 optimizations of antiaromatic states would require methods such as CASPT2, given that those based
 126 on a closed-shell reference do not describe correctly the biradical character. Such studies are outside
 127 the scope of the present work but may be considered when CASPT2 analytical gradients and Hessians
 128 become widely available, making the optimization and characterization of excited-state local minima
 129 and saddle points very much faster and more reliable.

131 2.2 Multicentre bond indices

132 Such indices were originally introduced [59, 60] as mono-, bi- tri- and generally k -centre
 133 contributions resulting at the closed-shell SCF or Kohn-Sham level of theory from the identity (1)

$$134 \quad Tr(PS)^k = 2^{(k-1)}N = \sum_A \Delta_A^{(k)} + \sum_{A<B} \Delta_{AB}^{(k)} + \sum_{A<B<C} \Delta_{ABC}^{(k)} + \dots + \sum_{A<B<C\dots K} \Delta_{ABC\dots K}^{(k)} \quad (1)$$

135 in which P and S denote the charge-density and overlap matrices, respectively, and N is the number
 136 of electrons. The usefulness of these indices for structural elucidations arises from the interesting
 137 nontrivial finding that their values mimic sensitively the presence and/or absence of bonding
 138 interactions between individual atoms in a molecule. Thus, for example, in the case of molecules that
 139 are well described by the familiar classical Lewis model of localized two-centre two-electron bonds,
 140 the corresponding 2-centre bond indices, which coincide in this case with the well-known Wiberg-
 141 Mayer indices [61, 62], attain non-negligible values only between classically bonded atoms while the
 142 corresponding values of the indices for pairs of classically nonbonded atoms are negligible. Such
 143 indices are also very useful for molecules whose description transcends the classical Lewis model by
 144

145 involving instead bonding interactions that are delocalized over more than two atomic centres. The
 146 indices retain the ability in such cases to detect and reveal just those atomic fragments engaged in the
 147 delocalized bonding, whereas the values for the remaining fragments are very small.

148 In various earlier papers the definition was modified [29, 63, 64] and the indices were instead
 149 normalized to N , as shown in Eq. (2).

150

$$\frac{1}{2^{(k-1)}} \text{Tr}(PS)^k = N = \sum_A \Delta_A^{(k)} + \sum_{A<B} \Delta_{AB}^{(k)} + \sum_{A<B<C} \Delta_{ABC}^{(k)} + \dots + \sum_{A<B<C\dots K} \Delta_{ABC\dots K}^{(k)} \quad (2)$$

151

152 A slight disadvantage of this alternative definition is that the resulting values of the indices tend to
 153 decrease rather dramatically with increasing k . We have thus chosen for the present work to use the
 154 original definition (Eq. (1)) in which the normalization sum is $\text{Tr}(PS)^k$ (which is equal to $2^{k-1}N$ at
 155 the closed-shell SCF level). Otherwise, even relevant indices would be rather small for $k > 3$. An
 156 obvious alternative to the different values returned by Eqs. (1) and (2) would be to quote instead the
 157 proportion of the quantity being “partitioned”.

158 In the case of k -centre indices the general definition (Eq. (1)) leads to Eq. (3)

159

$$MCI_{ABC\dots K} = \sum_i \sum_{\mu}^A \sum_{\nu}^B \sum_{\lambda}^C \dots \sum_{\tau}^K \Gamma_i[(PS)_{\mu\nu}(PS)_{\nu\lambda}(PS)_{\lambda\sigma}\dots(PS)_{\tau\mu}] \quad (3)$$

160 where Γ_i is the permutation operator that interchanges the basis function labels (Greek letters),
 161 thereby ensuring that the index includes all of the terms that correspond to different permutations of
 162 atomic labels.

163 The above general formula can also be straightforwardly extended beyond the scope of the
 164 Hartree-Fock approximation. The formula remains formally the same, except of course that the
 165 idempotent charge-density matrix is replaced by the corresponding correlated first-order density
 166 matrix [65, 66]. The normalization sum $\text{Tr}(PS)^k$ is of course no longer straightforwardly linked to
 167 the total number of electrons, as in the case of the closed-shell SCF approximation. The above
 168 definitions of multicentre indices that are based on a Mulliken-like partitioning can easily be
 169 generalized to the framework of QTAIM [67] analysis [30, 68], such that Eq. (4) is transformed to:

170

$$MCI_{ABC\dots K} = \sum_i \Gamma_i \left[\sum_{\alpha} \sum_{\beta} \sum_{\gamma} \dots \sum_{\tau} \eta_{\alpha} \eta_{\beta} \eta_{\gamma} \dots \eta_{\tau} \langle \alpha | \beta \rangle_A \langle \beta | \gamma \rangle_B \langle \gamma | \delta \rangle_C \dots \langle \tau | \alpha \rangle_K \right] \quad (4)$$

171

172 Here the symbol $\langle \lambda | \sigma \rangle_X$ denotes the domain-condensed overlap of natural orbitals λ and σ (*i.e.*
 173 integration over the QTAIM atomic domain of atom X), η_{λ} denotes the occupation number of λ , and
 174 the summations again run over all permutations of atomic labels.

175 Instead of using orbitals it is of course possible to calculate indices separately for α and β spin-
 176 orbitals. Such an approach was reported in earlier extensions of multicentre indices to open-shell
 177 systems [69]. The total index is of course then the sum of the corresponding α and β contributions.
 178 We note that a recent study dealing with the application of multicentre bond indices to the excited-
 179 state aromaticity of benzene and cyclobutadiene [47] used natural spin-orbitals (NSOs) instead of
 180 natural orbitals (NOs), even for singlet states. The multicentre indices (MCIs) reported in the present
 181 study were calculated with our own programs using the QTAIM approach [67], with the required
 182 domain-condensed overlaps generated using the AIMAll program [70].

183 Using NSO rather than NO expansions is of course straightforward for systems with nonzero
 184 spin because one may use combinations of the charge-density and spin-density matrices to generate
 185 the different NSO expansions for the α and β one-electron densities. On the other hand, the spin-
 186 density matrix is null for singlet states and so the NSO expansions of the α and β one-electron
 187 densities must coincide. Given that the NO occupations are split equally between the α and β NSOs
 188 we may refer to this as the “half-electron scheme”. Because the α and β NSOs are the same, and
 189 coincide with the NOs, the total α and β k -centre multicentre indices calculated using this scheme are

190 straightforwardly related to those calculated from the NO occupations (Eq. (4)) via the trivial scaling
 191 factor $\left(\frac{1}{2}\right)^{k-1}$.

192 A potential problem for singlet states can easily be appreciated by noticing that α and β NSO
 193 occupations do not distinguish between the combination of “singlet diradical” determinants $\varphi\bar{\psi}$ and
 194 $\bar{\varphi}\psi$ and the combination of “closed shell” determinants $\varphi\bar{\varphi}$ and $\psi\bar{\psi}$. As a consequence, the resulting
 195 multicentre indices do not take explicit account of which states have a high degree of diradical
 196 character and which of them do not. The degree of diradical character could of course be an important
 197 feature for considerations of aromaticity. As such the “half-electron” approach, although formally
 198 the correct one, might appear to be slightly questionable when considering, for example, an
 199 inherently diradical species such as the singlet ground state of square cyclobutadiene. As was
 200 demonstrated in the seminal study by Salem and Rowland [71], the diradicals represented in the
 201 simplest model by two degenerate orbitals occupied by two electrons form four electronic states,
 202 namely two biradical states (singlet and triplet) and two zwitterionic singlet states:

$$\begin{aligned} S_1, T_1 &= \frac{1}{\sqrt{2}}(|\phi\bar{\psi}\rangle \pm |\psi\bar{\varphi}\rangle) \\ Z_1 \pm Z_2 &= \frac{1}{\sqrt{2}}(|\varphi\bar{\varphi}\rangle \pm |\psi\bar{\psi}\rangle) \end{aligned} \quad (5)$$

203 Although all of these states differ at the level of the pair density, and thus also of the energy, all of
 204 the spinless one-electron densities coincide:

$$\rho(1) = \varphi^2(1) + \psi^2(1) \quad (6)$$

206
 207 Such observations made it seem attractive to consider taking explicit account of singlet diradical
 208 character by means of artificial modifications of the α and β NSO occupations. In the simple case of
 209 the singlet ground state of square cyclobutadiene, which features two singly occupied orbitals, we
 210 could for example consider that the first of them is pure α and the other one is pure β spin. We use
 211 the label “diradical scheme” for this somewhat artificial approach in which the α and β densities are
 212 now allowed to be different, albeit they still add to the correct total. In actual practice we did
 213 unfortunately find that manipulations of this sort were far from satisfactory. There were particular
 214 complications and uncertainties for cases such as states of benzene which feature two pairs of
 215 degenerate orbitals (each corresponding of course to one of the E irreducible representations in D_{6h}
 216 symmetry). We were also concerned that some invariances to orbital rotations might be lost and we
 217 noticed that using analogous manipulations for triplet states resulted in “artificial” NSO occupations
 218 that bear no obvious resemblance to the actual ones. As a consequence, we reluctantly mostly
 219 abandoned this diradical scheme and so we focus here on our results that were obtained for the
 220 singlet and triplet states with the actual NSO occupation numbers. Nonetheless, because of this
 221 inability of the first-order density matrix to reflect important features that are present in the
 222 wavefunction and the pair density, we considered it useful to take into account in our considerations
 223 also the eventual manifestation in the wavefunction of diradical character, given that it could be very
 224 important in the evaluation of the degree of aromaticity. For this purpose and in order to provide
 225 additional insights into the nature of the individual excited states of the molecules studied we also
 226 quantify the contributions to the occupation numbers that arise from diradical character. (Note that,
 227 instead of using the actual NSO occupations for the singlet states, we could have used Eq. (4) with
 228 the NO occupations, rescaling the resulting 4- and 6-centre indices by $1/8$ and $1/32$, respectively).

229 2.3 Similarity of excited states

230
 231 As an auxiliary tool to assess the aromaticity and/or antiaromaticity of individual excited states
 232 we also used a molecular similarity index that is based on the number of overlapping electrons
 233 (NOEL), as was introduced some time ago by Cioslowski [72]. In essence, the index of similarity
 234 between two molecules A and B is defined in terms of the first-order density matrices of the
 235 corresponding molecules as

236

$$d_{AB} = \int |\Gamma^A(x, x') - \Gamma^B(x, x')|^2 dx dx' \quad (7)$$

237
238 where the density matrices Γ^X are conveniently represented by NSO expansions. The smaller the
239 values of d_{AB} , the more similar are the first-order densities of the molecules *A* and *B*.

240 NOEL-based comparisons of systems with different geometries would involve also the
241 optimization of the mutual positions of the two molecules, so as to maximize the similarity. In the
242 present work, however, the comparisons of the different states of a given molecules are much more
243 straightforward because of our decision to consider vertical excitations, *i.e.* fixed geometries. The
244 above general formula then reduces to

$$d_{AB} = d_{AB}^\alpha + d_{AB}^\beta = \frac{Tr(P_A^\alpha S)(P_A^\alpha S) + Tr(P_B^\alpha S)(P_B^\alpha S) - 2Tr(P_A^\alpha S)(P_B^\alpha S) + Tr(P_A^\beta S)(P_A^\beta S) + Tr(P_B^\beta S)(P_B^\beta S) - 2Tr(P_A^\beta S)(P_B^\beta S)}{Tr(P_A^\alpha S)(P_A^\alpha S) + Tr(P_B^\alpha S)(P_B^\alpha S) - 2Tr(P_A^\alpha S)(P_B^\alpha S) + Tr(P_A^\beta S)(P_A^\beta S) + Tr(P_B^\beta S)(P_B^\beta S) - 2Tr(P_A^\beta S)(P_B^\beta S)} \quad (8)$$

246
247 where P_X^α and P_X^β denote the α and β one-electron density matrices, respectively, for a particular
248 electronic state of a given molecule and *S* is the overlap matrix.

249 3. Results and discussion

250 As our primary tool for the evaluation of excited-state aromaticity we used the multicentre bond
251 indices whose calculation requires knowledge of the first-order density matrix provided in a
252 quantum chemical calculation via natural orbitals and their occupation numbers. In view of the
253 potential problems mentioned in the previous section, the use of quantities based on the first-order
254 density matrix might not always be a completely satisfactory approach: This matrix is not able to
255 reflect all of the features of a more complicated wavefunction and, in certain cases, the features not
256 carried over could be of crucial importance. The relevance of this concern can be illustrated using
257 simple considerations applied to wavefunctions exhibiting diradical character which are often
258 encountered when describing excited electronic states.

259 It is of course entirely straightforward to construct an expansion of a CASSCF wavefunction in
260 terms of determinants built from NOs so as to reproduce the already known NO occupation numbers.
261 Then we can determine also the net contributions arising from determinants in which a particular
262 NO is singly occupied. Especially for singlet states, the results provide a useful quantitative measure
263 of the extent of diradical character. In most cases, sufficient qualitative information can be obtained
264 just by examining the compositions of the most important determinants in the expansion and, as
265 shown below, doing so is essential when evaluating the reliability of multicentre indices and NOEL-
266 based similarity values as aromaticity criteria.

267 The need for a more detailed analysis of the nature of each individual excited state is highlighted
268 by the observation that states of very different character can have fairly similar patterns of NO
269 occupation numbers, as can be seen in Tables 1–3. Such similarities are displayed, for example, by the
270 S_1 and S_2 states of benzene, as well as by all three singlet states of square cyclobutadiene that we
271 examined. The absence of pronounced differences between the patterns of NO occupation numbers
272 is a cause for concern because it is not clear how the multicentre indices, as well as the NOEL-based
273 d_{AB} values, will be able to distinguish properly between such electronic states unless the shapes of
274 the NOs change sufficiently between states.

275 The net contributions from all determinants in which a particular NO is singly occupied to the
276 wavefunctions for the various electronic states of benzene, square cyclobutadiene and disulfur
277 dinitride are shown in Tables 1–3. Clearly, both the S_1 state and, of course, the T_1 state of benzene
278 exhibit significant levels of diradical character, unlike the S_0 and S_2 states (see Table 1). In the case of
279 square cyclobutadiene (Table 2) the states with significant levels of diradical character are S_0 and
280 again, of course, T_1 , whereas there only minor traces of such character in the S_1 and S_2 states which
281 appear to be zwitterionic [71]. Moving on to S_2N_2 , we can see from Table 3 that that it is only the S_0
282 ground state that has slight diradical character, whereas there is strong diradical character in both of

283 the excited states. Inspection of the symmetries of the NOs for the electronic states of this molecule
 284 reveals that whereas the dominant diradical character in T₁ comes from two unpaired π electrons,
 285 much as in the corresponding states of C₆H₆ and C₄H₄, that in the S₁ state is associated with the
 286 coupling of an unpaired σ electron to an unpaired π electron. Therefore, we can expect that the
 287 NOEL-based similarity index for S₂N₂ will show significant differences between the valence σ system
 288 of the S₁ state and those of the S₀ and T₁ states.

289 **Table 1.** Active-space NO occupation numbers for the S₀, S₁, S₂ and T₁ states of C₆H₆ and active-space
 290 NSO occupation numbers for the T₁ state (all in descending order). Values in brackets show the net
 291 contributions from all determinants in which a particular NO is singly occupied.

	S ₀	S ₁	S ₂	T ₁	T ₁	
					α	β
η_1	1.961 (0.028)	1.863 (0.107)	1.952 (0.039)	1.910 (0.078)	0.986	0.924
η_2	1.902 (0.046)	1.445 (0.500)	1.494 (0.051)	1.464 (0.487)	0.966	0.498
η_3	1.902 (0.046)	1.445 (0.500)	1.494 (0.051)	1.464 (0.487)	0.966	0.498
η_4	0.100 (0.046)	0.569 (0.500)	0.524 (0.051)	0.536 (0.487)	0.503	0.034
η_5	0.100 (0.046)	0.569 (0.500)	0.524 (0.051)	0.536 (0.487)	0.503	0.034
η_6	0.036 (0.028)	0.109 (0.087)	0.012 (0.007)	0.090 (0.079)	0.077	0.013

292 **Table 2:** Active-space NO occupation numbers for the S₀, S₁, S₂ and T₁ states of square C₄H₄ and active-
 293 space NSO occupation numbers for the T₁ state (all in descending order). Values in brackets show the
 294 net contributions from all determinants in which a particular NO is singly occupied.

	S ₀	S ₁	S ₂	T ₁	T ₁	
					α	β
η_1	1.905 (0.073)	1.835 (0.031)	1.994 (0.001)	1.914 (0.072)	0.993	0.921
η_2	1.000 (1.000)	1.005 (0.000)	1.000 (0.000)	1.000 (1.000)	0.964	0.036
η_3	1.000 (1.000)	1.005 (0.000)	1.000 (0.000)	1.000 (1.000)	0.964	0.036
η_4	0.095 (0.073)	0.155 (0.031)	0.006 (0.001)	0.086 (0.072)	0.079	0.007

295 **Table 3:** Active-space NO occupation numbers for the S₀, S₁ and T₁ states of S₂N₂ and active-space
 296 NSO occupation numbers for the T₁ state (all in descending order). Values in brackets show the net
 297 contributions from all determinants in which a particular NO is singly occupied.

	S ₀	S ₁	T ₁	T ₁	
				α	β
η_1	1.997 (0.002)	1.997 (0.002)	1.998 (0.002)	0.999	0.999
η_2	1.997 (0.002)	1.996 (0.003)	1.997 (0.002)	0.999	0.998
η_3	1.996 (0.003)	1.994 (0.005)	1.995 (0.004)	0.999	0.998
η_4	1.991 (0.005)	1.990 (0.007)	1.994 (0.006)	0.998	0.996
η_5	1.986 (0.012)	1.984 (0.013)	1.993 (0.005)	0.998	0.994
η_6	1.981 (0.016)	1.968 (0.025)	1.983 (0.016)	0.997	0.991
η_7	1.980 (0.010)	1.965 (0.028)	1.982 (0.015)	0.997	0.984
η_8	1.964 (0.028)	1.960 (0.031)	1.967 (0.027)	0.996	0.983
η_9	1.962 (0.030)	1.960 (0.035)	1.965 (0.024)	0.991	0.983
η_{10}	1.960 (0.030)	1.911 (0.034)	1.965 (0.025)	0.984	0.982
η_{11}	1.908 (0.030)	1.009 (0.979)	1.014 (0.984)	0.983	0.017
η_{12}	0.126 (0.047)	0.995 (0.970)	1.008 (0.986)	0.983	0.017
η_{13}	0.041 (0.031)	0.126 (0.060)	0.037 (0.026)	0.019	0.016
η_{14}	0.040 (0.029)	0.058 (0.045)	0.037 (0.026)	0.019	0.016
η_{15}	0.038 (0.030)	0.044 (0.032)	0.035 (0.026)	0.019	0.014
η_{16}	0.033 (0.024)	0.043 (0.031)	0.031 (0.022)	0.017	0.012

298 **Table 4:** 6-centre MCIs for the S_0 , S_1 , S_2 and T_1 states of C_6H_6 , 4-centre MCIs for the S_0 , S_1 , S_2 and T_1
 299 states of square C_4H_4 and 4-centre MCIs for the S_0 , S_1 and T_1 states of S_2N_2 . QTAIM/6-311++G(2d,2p)
 300 for C_6H_6 and C_4H_4 ; QTAIM/cc-pVTZ for S_2N_2 . Values in brackets show the π -only (C_6H_6 and C_4H_4)
 301 and π -only valence (S_2N_2) components of the total index.

	C_6H_6	C_4H_4	S_2N_2
S_0	0.0160 (0.0159)	0.0360 (0.0336)	0.0525 (0.0504)
S_1	0.0016 (0.0014)	0.0263 (0.0240)	0.0128 (0.0164)
S_2	0.0029 (0.0027)	0.0477 (0.0454)	
T_1	0.0030 (0.0029)	0.0774 (0.0749)	-0.0045 (-0.0069)

302
 303 The values of multicentre QTAIM indices for C_6H_6 , C_4H_4 and S_2N_2 calculated using NSOs are
 304 shown in Table 4. For singlet states we have used the actual NSO occupations, *i.e.* the "half-electron"
 305 scheme. While inspecting the numbers in this table, it is useful to adopt the largest total 6-centre MCI
 306 value of 0.016 for the archetypal example of an aromatic system, the ground state of benzene, as a
 307 yardstick for assessing the values of this index for the other states of this molecule. Whereas the value
 308 of the index for the first excited singlet state is smaller than its S_0 counterpart by an order of
 309 magnitude, those for the S_2 and T_1 states which turn out to very close are, instead, smaller by a factor
 310 of about five. It should be mentioned that, in keeping with expectations, the total values of the indices
 311 are dominated by their π -only components for all of the states included in Table 4. The situation in
 312 the case of S_2N_2 is similar to that in C_6H_6 : Once again, the largest value of the 4-centre MCI is that for
 313 the ground state, whereas the excited-state indices are considerably smaller. The 4-centre MCIs for
 314 the electronic states of square C_4H_4 follow a different pattern: The largest value corresponds to the
 315 lowest triplet state T_1 , whereas the indices for the three singlet states are considerably smaller.

316 The changes in the values of the MCIs in Table 4 between S_0 and T_1 states are fully consistent
 317 with Baird's original rule [42] which addresses aromaticity reversals involving the singlet ground
 318 and lowest triplet electronic states only. However, when singlet states come into play, there are some
 319 notable discrepancies from the behaviour expected on the basis of the results from previous studies
 320 which discuss in detail ground- and excited-state magnetic properties, including several types of
 321 NICS [44, 45, 52]. Let us start with benzene. The S_1 state of C_6H_6 is correctly classified as antiaromatic,
 322 with S_1 being more antiaromatic than T_1 which is in line with predictions based on magnetic
 323 properties [44, 45] and several multicentre and delocalization indices [47]. However, S_2 in C_6H_6 is
 324 predicted to be just as antiaromatic as T_1 whereas the magnetic properties of this state, calculated at
 325 the same geometry and level of theory, strongly suggest that it is even more aromatic than the ground
 326 state S_0 [44]. Incidentally, S_2 in C_6H_6 was classified as more antiaromatic than S_1 in [47] but this was
 327 due to analysing the doubly-degenerate S_4 rather than S_2 (for details, see [44]). We continue our
 328 analysis with square C_4H_4 . According to the 4-centre MCI values, S_1 is the most antiaromatic state of
 329 this molecule whereas the isotropic shielding isosurface for this state and other magnetic properties,
 330 calculated at the same geometry and level of theory, show clearly that it is aromatic [44]. S_2 is
 331 predicted to be less antiaromatic than S_0 which is in agreement with the results of magnetic property
 332 calculations [44, 45]. Finally, according to the respective 4-centre MCI values, in S_2N_2 S_1 is less
 333 antiaromatic than T_1 whereas magnetic property calculations suggest the opposite ordering for these
 334 two states [52]. One further observation is that the values of the 6-centre MCI for benzene are, for
 335 most states, of smaller magnitude than the corresponding 4-centre MCIs for square cyclobutadiene
 336 and disulfur dinitride, which precludes comparisons between MCIs for different rings.

337 The discrepancies between the current MCI-based assessments of the aromaticities of singlet
 338 excited states and those coming from calculations of various magnetic second-order response
 339 properties [44, 45] underline our concerns as to whether first-order density-based indices are capable
 340 of reflecting more subtle effects whose description relies on the more detailed information inherent
 341 to wavefunctions or pair densities for particular electronic states.

342 Similar concerns are associated with comparisons utilizing the NOEL-based quantity d_{AB} . This
 343 quantity was originally designed [72] as a quantitative measure of the similarity between the electron
 344 densities of different molecules but in this study we use it to investigate the similarity between the

345 electron densities of different excited states of one molecule. The values of the NOEL-based similarity
 346 index d_{AB} for the low-lying electronic states of benzene, square cyclobutadiene and disulfur
 347 dinitride, calculated using NSOs, are summarized in Tables 5–7. These results demonstrate clearly,
 348 in keeping with expectations, that the total d_{AB} indices for C_6H_6 and C_4H_4 are, in all cases, dominated
 349 by their π -only components. In the case of S_2N_2 , d_{AB} indices involving the S_1 state show large σ
 350 contributions due to the composition of the wavefunction for this state (see above).

351 **Table 5:** Similarity indices d_{AB} calculated at the CASSCF(6,6)/6-311++G(2d,2p) level for low-lying
 352 electronic states of C_6H_6 . Values in brackets are π -only contributions to the total index.

State	S ₁	S ₂	T ₁
S ₀	0.4402 (0.4396)	0.3639 (0.3612)	0.8323 (0.8319)
S ₁		0.0453 (0.0433)	0.4465 (0.4464)
S ₂			0.4866 (0.4842)

353

354 **Table 6:** Similarity indices d_{AB} calculated at the CASSCF(4,4)/6-311++G(2d,2p) level for low-lying
 355 electronic states of square C_4H_4 . Values in brackets are π -only contributions to the total index.

State	S ₁	S ₂	T ₁
S ₀	0.0121 (0.0117)	0.0557 (0.0532)	0.8672 (0.8672)
S ₁		0.0417 (0.0408)	0.8754 (0.8752)
S ₂			0.9086 (0.9067)

356 **Table 7:** Similarity indices d_{AB} calculated at the CASSCF(22,16)/cc-pVTZ level for low-lying
 357 electronic states of S_2N_2 . Values in brackets are (π -only, σ -only) valence contributions to the total
 358 index.

State	S ₁	T ₁
S ₀	0.9596 (0.4796, 0.4799)	1.8061 (1.7896, 0.0166)
S ₁		2.8024 (2.2926, 0.5098)

359

360 The data in Table 5 suggest some similarity between the S_0 and S_2 states of benzene, in line with the
 361 expected aromaticity of S_2 [44], as well as very little similarity between the S_0 and T_1 states, in
 362 agreement with Baird's rule. However, the surprisingly high level of similarity between the S_1 and S_2
 363 states which have been classified as antiaromatic and aromatic, respectively [44], is very much out of
 364 line with the rather different magnetic properties of these states. Somewhat surprising are also the
 365 comparable levels of similarity between the S_1 and T_1 states, both of which are supposed to be
 366 antiaromatic, and the S_2 and T_1 states which are supposed to be aromatic and antiaromatic,
 367 respectively [44].

368 Other similarity assessments of questionable utility can be found amongst the data for square
 369 cyclobutadiene that are presented in Table 6, starting with the high level of similarity between the S_0
 370 and S_1 states which is unexpected, in view of the predicted aromaticity reversal between these states
 371 [44]. Both S_1 and T_1 are expected to be aromatic [44], but the level of similarity between these states is
 372 comparable to that between S_2 and T_1 which are expected to be antiaromatic and aromatic,
 373 respectively.

374 The d_{AB} indices are doing a better job in the case of S_2N_2 (see Table 7): S_0 and S_1 are quite
 375 dissimilar, and so are S_0 and T_1 , as expected for comparisons between wavefunctions corresponding
 376 to aromatic and antiaromatic states. S_1 and T_1 come out as very dissimilar which is not unrealistic, as
 377 these states have been predicted to show very different levels of antiaromaticity [52]. As has been

378 mentioned, the σ -only valence contributions to d_{AB} are large in all comparisons involving the first
379 singlet excited state, due to the composition of the S_1 wavefunction (see above).

380 We have shown that the multicentre indices (MCIs) examined in this work perform well for
381 aromaticity reversals involving the singlet ground and lowest triplet electronic states which are
382 covered by Baird's original rule [42]. Our attempts to apply these indices to aromaticity reversals
383 involving singlet excited states were less satisfactory. While this may seem disappointing, since
384 aromaticity/antiaromaticity switching can be predicted even using simple topological resonance
385 energies [43], it should be emphasized that TRE-based studies do not distinguish between singlet and
386 triplet excited states, and all MCI problems arise when dealing with singlet excited states. When
387 dealing with singlet ground states, 6-centre indices have been found to correlate very well with the
388 energetic stabilization resulting from cyclic delocalization in individual benzene rings in polycyclic
389 aromatic hydrocarbons [29,40]; multicentre indices have also been reported as a reliable measure of
390 aromaticity in all-metal clusters [73].

391 One potential source of the problems experienced when trying to apply multicentre indices to
392 singlet excited states can be associated with the reasons behind the very good performance of MCIs
393 for the ground states of polycyclic aromatic hydrocarbons. The correlation between MCIs and
394 energetic stabilization stems from Coulson's integral formula [74] which describes quantitatively the
395 extent of energetic stabilization/destabilization associated with cyclic conjugation. However, this
396 formula can be applied only to the ground states of conjugated hydrocarbons and, as there is no
397 equivalent formula for excited states, there is also no straightforward way of measuring the energetic
398 effects resulting from cyclic conjugation in other than ground states (TRE is applicable only to the
399 lowest excited state). The absence of an energy-based justification of excited-state MCIs may have
400 adverse impact on their performance in comparison to ground-state MCIs. On the other hand, cyclic
401 conjugation in excited states can be thought to induce excited-state ring currents and the nature of
402 these currents (paratropic *vs* diatropic) is decisive for excited aromaticity. These ring currents can be
403 integrated using the Bio-Savart law (as shown, for example, in [75]), producing excited-state magnetic
404 shielding tensors such as those calculated and analysed in [44, 45, 46, 52] which explains why the
405 magnetic properties of excited states provide reliable measures of excited-state aromaticity.

406 In addition to these somewhat qualitative arguments, more detailed theoretical considerations
407 can be used to identify additional factors affecting the performance of the multicentre indices for
408 singlet excited states. For this purpose, it is useful to refer again to the paper by Salem and
409 Rowland [71] dealing with the electronic structure of diradicals. As we mentioned previously,
410 although all four biradical and zwitterionic states for the simple two-orbital model (see Eq. (5)) differ
411 in energy (and, consequently, in wavefunction and in pair density), their one-electron densities are
412 exactly the same. One straightforward implication is that the first-order density matrices for different
413 electronic states of real systems could omit important details, the absence of which would result in
414 multicentre indices giving misleading information about the extent of similarity between these states.
415 Although the discussion in [71] is focused on inherently diradical species, similar problems, arising
416 from details not available within the first-order density matrix, are apparently more general since, as
417 demonstrated in this study, partial diradical character is evident even in the excited-state
418 wavefunctions of a paradigmatic molecule such as benzene. On the other hand, the undeniable
419 usefulness of multicentre indices as a measure of ground-state aromaticity [29, 30, 32, 40, 73] can be
420 attributed to the fact that, at the closed-shell SCF and Kohn-Sham levels of theory, the first-order
421 density matrix determines all higher-order densities so that energy-related quantities are described
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423
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425 and D.L.C. wrote independent program codes and computed all indices independently. P.B.K. helped with the
426 CASSCF calculations. R.P. wrote the manuscript. D.L.C and P.B.K. helped with analyzing the results and writing
427 the manuscript. All authors have read and agreed to the published version of the manuscript.

428
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430

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593