

# Electron Delocalization and Aromaticity in Low-Lying Excited States of Archetypal Organic Compounds

*Ferran Feixas,<sup>a\*</sup> Jelle Vandebussche,<sup>b</sup> Patrick Bultinck,<sup>b</sup> Eduard Matito<sup>c</sup> and Miquel Solà<sup>a\*</sup>*

a) Institut de Química Computacional and Departament de Química, Universitat de Girona, Campus Montilivi, 17071 Girona, Catalonia, Spain

b) Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), 9000 Gent, Belgium

c) Kimika Fakultatea, Euskal Herriko Unibertsitatea and Donostia International Physics Center (DIPC), P.K. 1072, 20018 Donostia, Euskadi, Spain

Corresponding authors e-mail address: ferran.feixas@gmail.com, miquel.sola@udg.edu

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## Abstract

Aromaticity is a property usually linked to the ground state of stable molecules. Although it is well-known that certain excited states are unquestionably aromatic, the aromaticity of excited states remains rather unexplored. To move one step forward in the comprehension of aromaticity in excited states, in this work we analyze the electron delocalization and aromaticity of a series of low-lying excited states of cyclobutadiene, benzene, and cyclooctatetraene with different multiplicities at the CASSCF level by means of electron delocalization measures. While our results are in agreement with Baird's rule for the aromaticity of the lowest-lying triplet excited state in annulenes having  $4n\pi$ -electrons, they do not support Soncini and Fowler's generalization of Baird's rule pointing out that the lowest-lying quintet state of benzene and septet state of cyclooctatetraene are not aromatic.

## Introduction

Aromaticity is a property usually attributed to the ground state of stable molecules with a cyclic electronic delocalization that confers extra stability, bond length equalization, unusual reactivity, particular spectroscopic characteristics, and distinctive magnetic properties related to strong induced ring currents.<sup>1</sup> It is now well-accepted that not only the ground states of certain stable species but also the ground state of some transition states (TSs) are aromatic. Indeed, already in 1938, Evans and Warhurst<sup>2</sup> noted the analogy between the  $\pi$ -electrons of benzene and the six delocalized electrons in the cyclic TS of the Diels-Alder reaction of butadiene and ethylene. It is nowadays widely accepted that most thermally allowed pericyclic reactions take place preferentially through concerted aromatic TSs.<sup>3</sup>

On the other hand, the aromaticity of excited states has been much less explored. From an experimental point of view, this is due to the inherent difficulty to study the molecular structure, stability, reactivity, and the magnetic and spectroscopic properties of classical organic molecules in their excited states. From a theoretical point of view, what complicate matters is, first, the fact that the correct treatment of excited states requires the use of sophisticated multiconfigurational methods and, second, it is not clear whether the usual reference compound used by many indicators of aromaticity, i.e., the ground state of benzene or related molecules, is still a valid reference for excited states.

The first evidence of aromaticity in excited states can be traced back to the work by Baird. Using perturbational molecular orbital theory he showed that annulenes that are antiaromatic in their singlet ground state are aromatic in their lowest-lying triplet state and vice versa for annulenes that are aromatic in the ground state.<sup>4</sup> The identification<sup>5</sup> of the planar triplet ground states of  $C_5H_5^+$  and  $C_5Cl_5^+$  as well as a recent

photoelectron spectroscopic study<sup>6</sup> of the first singlet and triplet states of  $C_5H_5^+$  provided experimental support for Baird's hypothesis of triplet-state aromaticity. The validity of Baird's rule (cyclic conjugated compounds with  $4n\pi$ -electrons are aromatic in their lowest-lying triplet state,  $T_1$ ) was substantiated theoretically by Fratev et al. who showed that the equilibrium structure of the  $T_1$  state of cyclobutadiene presents bond length equalization and  $D_{4h}$  symmetry.<sup>7</sup> As pointed out by these authors,<sup>7</sup> the aromaticity of this  $T_1$  state concurs with the relative stability of photochemically-obtained cyclobutadiene.<sup>8</sup> More recently, the triplet state  $4n\pi$  Baird rule was confirmed through nucleus-independent chemical shifts (NICS), magnetic susceptibility, and aromatic stabilization energy calculations by Schleyer *et al.*<sup>9</sup> as well as from the study of ring currents in  $4n\pi$ -electron monocycles.<sup>10</sup> In the work by Gogonea and coworkers it was also found that the  $T_1$  state of  $C_4H_4$ ,  $C_5H_5^+$ ,  $C_7H_7^-$ , and  $C_8H_8$  was aromatic, the optimized geometry being of  $D_{nh}$  symmetry with C–C bond lengths close to those of benzene.<sup>9b</sup> Finally, a recent theoretical work<sup>11</sup> based on the analysis of the bifurcation of the  $\pi$ -contribution to the electron localization function (ELF) for the lowest-lying triplet state of  $4n\pi$ -electron monocycles provided additional support to the validity of Baird's rule. Moreover, triplet state aromaticity was applied to rationalize the stability of substituted fulvenes,<sup>12</sup> and the dipole moments of fulvenes, fulvalenes, and azulene.<sup>13</sup>

The excited state aromaticity is not only ascribed to triplet state aromaticity for  $4n$  monocycles. For instance, the lowest-lying singlet excited state ( $S_1$ ) of square cyclobutadiene and cyclooctatetraene was reported to be aromatic by Zilberg and Haas<sup>14</sup> and by Karadakov<sup>15</sup> using NICS measures at the CASSCF level.<sup>16</sup> More recently, excited state aromaticity has been found in the lowest-lying singlet excited state of fulvene derivatives.<sup>17</sup> It is usually accepted that  $4n\pi$ -electron monocycles are aromatic not only in the  $T_1$  (Baird's rule) but also in the  $S_1$  state. Finally, let us mention the work

by Soncini and Fowler that represents a generalized form of Baird's rule.<sup>18</sup> Using an orbital model for the electronic currents, Soncini and Fowler concluded that the lowest-lying electronic states with even spin (singlet, quintet,...) of rings with  $(4n+2)\pi$ -electrons and the lowest-lying states with odd spin (triplet, septet,...) of monocycles with  $4n\pi$ -electrons are aromatic.

In the present work, we aim to explore aromaticity and antiaromaticity in the lowest-lying excited states in a series of simple annulenes by means of electron delocalization measures. The literature on this topic is very scarce and mostly uses NICS indicators to discuss aromaticity. In this regard, we believe<sup>16</sup> that other aromaticity measures of this phenomena should be used to confirm and complement the results obtained from NICS. We will analyze multicenter indices, which are among the most reliable indicators of aromaticity.<sup>19</sup>

## **Methodology**

The concept of aromaticity has been linked to cyclic electron delocalization from the very beginning. Consequently, the understanding of electron delocalization patterns of aromatic and antiaromatic compounds became a primary concern. In this work we measure the electron delocalization by means of so-called electron sharing indices (ESI),<sup>20</sup> which are also known as delocalization indices (DI)<sup>20a, 21</sup> and measure the extent of delocalization between a pair of either bonded or non-bonded atoms. It is worth noting here that the ESI concept has been recently reformulated by Bultinck et al. from a purely density matrix approach.<sup>22</sup> The generalization of the ESI to more than two atoms led to the definition of the multicenter indices.<sup>23</sup> Aromaticity descriptors based on both delocalization and multicenter indices perform remarkably well in the ground state of organic compounds.<sup>19b</sup> In the present work we will use them for the first time to

quantify the electron delocalization in the low-lying excited states of aromatic and antiaromatic compounds. Although several partitions can be used to define the atomic regions needed to calculate the ESI values, we have made use of the molecular partition based on the quantum theory of the atoms in molecules (QTAIM)<sup>24</sup> because they give more reasonable ESI values<sup>25</sup> and they are more adequate for aromaticity studies.<sup>26</sup>

The ESI between atoms A and B,  $\delta(A,B)$  has been obtained by double integration of the exchange-correlation density,  $\gamma_{XC}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2)$ ,<sup>27</sup>

$$\gamma_{XC}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2) = \gamma^{(2)}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2) - \rho(\vec{\mathbf{r}}_1)\rho(\vec{\mathbf{r}}_2) . \quad (1)$$

over the regions that correspond to atoms A and B,

$$\delta(A,B) = -2 \int_A \int_B \gamma_{XC}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2) d\vec{\mathbf{r}}_1 d\vec{\mathbf{r}}_2 . \quad (2)$$

Since the pair density of Eq. (1) can be exactly separated in terms of its spin cases as:

$$\gamma^{(2)}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2) = \gamma^{(2)\alpha\alpha}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2) + \gamma^{(2)\alpha\beta}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2) + \gamma^{(2)\beta\alpha}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2) + \gamma^{(2)\beta\beta}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2) , \quad (3)$$

it is possible to separate the exchange-correlation density and  $\delta(A,B)$  in their spin cases.

For **single determinant** wavefunctions (including density functional approaches),  $\delta(A,B)$  is expressed in terms of atomic overlaps as

$$\delta(A,B) = 2 \sum_{i,j}^{occ.MSO} S_{ij}(A)S_{ij}(B) , \quad (4)$$

where the sum runs over all occupied molecular spin-orbitals (MSOs).  $S_{ij}(A)$  are the elements of the atomic overlap matrix (AOM) that represent the overlap between MSO  $i$  and  $j$  within the region of the atom  $A$  defined in the framework of the QTAIM.  $S_{ij}(A)$  equals zero if the spin orbitals have different spins. Since in this work we deal with correlated wavefunctions obtained at the CASSCF level of theory, the **single determinant** approach is not suitable. For correlated wavefunctions the ESI requires the calculation of the expensive second-order reduced density matrix (2-RDM),  $\gamma^{(2)}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2)$ ,

which represents the bottleneck of the calculation and limits the use of DI to small systems. The expression that has to be calculated in this case is:

$$\delta^{xct}(A,B) = -2 \sum_{i,j,k,l}^{MSO} \Gamma_{ij}^{kl} S_{ij}(A) S_{kl}(B) + 2N(A)N(B) \quad . \quad (5)$$

Eq. (5) is strictly applicable in variational expansion methods and it should not be used with **perturbational** approaches.<sup>28</sup> Over the last years, many approximated definitions of the ESI based on first order reduced density matrices (1-RDM) have been proposed in order to avoid the computation of  $\gamma^{(2)}(\vec{r}_1, \vec{r}_2)$ . In particular, in this work we focus our attention on the expressions that make use of natural orbitals and their respective occupancies.<sup>20c, 21b-d</sup> In 1993, Fulton suggested to calculate the extent of electron sharing between a pair of atoms<sup>21b</sup> as follows:

$$\delta^F(A,B) = 2 \sum_{i,j}^{occ.NSO} \lambda_i^{1/2} \lambda_j^{1/2} S_{ij}(A) S_{ij}(B) \quad , \quad (6)$$

where  $\lambda_i^{1/2}$  are the square root of the natural occupancies of the corresponding natural spin orbitals (NSO) and  $S_{ij}(A)$  are the elements of the AOM of the NSO integrated over the region of the atom A. One year later, Ángyán and coworkers introduced another ESI based on the exchange part of the 2-RDM for **single determinant** wavefunctions within the framework of the QTAIM that can be written as:

$$\delta^A(A,B) = 2 \sum_{i,j}^{occ.NSO} \lambda_i \lambda_j S_{ij}(A) S_{ij}(B) \quad . \quad (7)$$

All these expressions, Eqns (4-7), are equivalent for **single determinant** wavefunctions.

In the present work, we have used two indicators of aromaticity based on the above-mentioned ESI. The main aim of these descriptors is to measure the amount of cyclic electron delocalization, which is associated with the aromaticity of the ring. First, the para-delocalization index (PDI) is calculated as an average of all DIs of para-related

carbon atoms of a given six-membered ring (6-MR).<sup>29</sup> Second, the aromatic fluctuation index (FLU) takes into account the amount of electron sharing between bonded pairs of atoms and the similarity between adjacent atoms.<sup>30</sup> Let us now consider a ring structure of  $N$  atoms represented by the following string  $A = \{A_1, A_2, \dots, A_N\}$ , where the elements are ordered according to the connectivity of the atoms in a ring. Then, FLU is given by:

$$FLU(\mathcal{A}) = \frac{1}{N} \sum_{i=1}^N \left[ \left( \frac{V(A_i)}{V(A_{i-1})} \right)^\alpha \left( \frac{\delta(A_i, A_{i-1}) - \delta_{ref}(A_i, A_{i-1})}{\delta_{ref}(A_i, A_{i-1})} \right) \right]^2, \quad (8)$$

where  $A_0 \equiv A_N$  and half the value of  $V(A)$  is recognized by some authors as the atomic valence defined as:

$$V(A_i) = \sum_{A_j \neq A_i} \delta(A_i, A_j) \quad , \quad (9)$$

and  $\alpha$  is a simple function to make sure that the first term in Eq. (8) is always greater or equal to 1, thus taking the values:

$$\alpha = \begin{cases} 1 & V(A_i) > V(A_{i-1}) \\ -1 & V(A_i) \leq V(A_{i-1}) \end{cases} \quad . \quad (10)$$

The  $\delta_{ref}(C, C)$  reference values are  $\delta_{ref}^F(C, C) = 1.288e$  and  $\delta_{ref}^A(C, C) = 1.341e$  that correspond to the DI value of benzene in its ground state at the CASSCF(6,6)/6-311++G(d,p) level of theory for the Fulton and Ángyán indices. FLU is close to 0 in aromatic species, and differs from it in non-aromatic ones. The main disadvantages of PDI and FLU are that the former is limited to 6-MR while the latter depends on references values that limit its use to organic systems and cannot be use in the study of chemical reactivity.<sup>31</sup>

The use of multicenter indices has gained popularity as a tool to analyze aromaticity of both organic and inorganic systems.<sup>19, 23c, 31b, 32</sup> For the analysis of the



aromatic character of the low-lying excited states we have made use of the  $I_{ring}$  and the multicenter index (MCI).<sup>23c, 33</sup> These indices can be applied to rings of different sizes and with the presence of different atoms including metals.<sup>34</sup> The  $I_{ring}$  index was defined by Giambiagi et al. as:<sup>35</sup>

$$I_{ring}(\mathcal{A}) = \sum_{i_1, i_2, \dots, i_N} n_{i_1} \mathbf{L} n_{i_N} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \mathbf{L} S_{i_{N-1} i_N}(A_N) \quad (11)$$

$n_i$  being the occupancy of molecular orbital  $i$ . This expression is used both for closed-shell and open-shell species, and **single determinant** and correlated wavefunctions. In this latter case, NSO occupations and overlaps are used in Eq. (11). The result is an approximation to the exact result that could be obtained using an Nth order reduced density matrix and corresponds to the N-order central moment of the electron population.<sup>36</sup> This formula is the equivalent in the multicenter case to the Ángyán DIs for two-center indices. Summing up all the  $I_{ring}$  values resulting from the permutations of indices  $A_1, A_2, \dots, A_N$  the mentioned MCI index<sup>33</sup> is defined as:

$$MCI(\mathcal{A}) = \frac{1}{2N} \sum_{P(\mathcal{A})} I_{ring}(\mathcal{A}) \quad (12)$$

where  $P(A)$  stands for a permutation operator which interchanges the atomic labels  $A_1, A_2, \dots, A_N$  to generate up to the  $N!$  permutations of the elements in the string  $\mathcal{A}$ .<sup>23c, 37</sup> In general, the tendency is that the more positive the  $I_{ring}$  and MCI values are,<sup>38</sup> the more aromatic the ring is.

All calculations have been performed with the Gaussian 03 package.<sup>39</sup> The optimized geometries have been obtained in the framework of the complete active space self-consistent field (CASSCF) level of theory. The 6-311++G(d,p) basis set has been used for all calculations.<sup>40</sup> Despite this basis set gives a nonplanar benzene geometry for some methods such as MP2,<sup>41</sup> at the CASSCF level of theory the planar geometry of

benzene is well-reproduced. The active space used for the calculations will be specified for each particular case in the results section. To evaluate the aromaticity of the lowest-lying singlet and triplet states we have performed vertical excitations from the ground state global minima or from other relevant critical points using state-averaged calculations (SA-CASSCF). In some particular cases, we have also optimized the geometry of the excited states in order to analyze the effect of the geometry and wavefunction relaxation. Calculation of atomic overlap matrices and computation of DI, PDI, FLU, and multicenter indices has been performed with the AIMPAC<sup>42</sup> and the ESI-3D<sup>43</sup> collection of programs.<sup>44</sup> To assess the performance of Fulton and Ángyán approximations of DI at the lowest-lying excited states, we have computed the  $\gamma^{(2)}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2)$  in order to calculate the *exact* ESI for a set of small systems (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and CH<sub>2</sub>O). The corresponding exact 2-RDMs have been obtained with DMn program.<sup>45</sup>

In some cases, we have also performed B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) calculations to discuss the aromaticity in the singlet, triplet, quintet or septet lowest-lying states. Since the electron-pair density is not available at the B3LYP level of theory,<sup>46</sup> as an approximation we have used the Kohn-Sham orbitals obtained from a DFT calculation to compute Hartree-Fock-like DIs. The values of the DIs obtained using this approximation are generally closer to the Hartree-Fock (HF) values (especially for non-polarized bonds) than correlated DIs obtained with a configuration interaction method values (see Supporting Information for DIs computed at the HF level).

## Results and discussion

The results section is organized as follows. First, we analyze the performance of Fulton and Ángyán indices to include the electron correlation in the DI value in the lowest-lying singlet states of some small organic molecules such as  $C_2H_4$ ,  $C_2H_2$ , and  $CH_2O$ . Second, the values of FLU, PDI,  $I_{ring}$ , and MCI are calculated for the lowest-lying singlet and triplet states of a series of simple annulenes, i.e.  $C_4H_4$ ,  $C_6H_6$ , and  $C_8H_8$ . In some cases, the values of lowest-lying quintet and septet states are also reported.

### A. Preliminary considerations: Electron delocalization measures in excited states

The calculation of DIs at a correlated level has been extensively discussed for a large list of molecules in the ground state. In particular, some of us compared the values of exact DIs obtained using Eq. (5) from the 2-RDM calculated at the CISD level of theory with the approximated ones using the 1-RDM, namely,  $\delta^F(A,B)$  and  $\delta^A(A,B)$  indices (Eqs. (6) and (7)), concluding that the approximation proposed by Fulton includes better the electron correlation effects from the 2-RDM than the Ángyán index.<sup>20c</sup> On the other hand, studies that analyze DI values in the excited states are scarcer. In 1999, Ángyán et al. discussed the concept of an electron sharing index for correlated wavefunctions, although they focused on the ground state, they underlined the importance of analyzing the performance of different definitions of DI in excited states.<sup>47</sup> It is worth noting that one of the first attempts to calculate the electron sharing between two atoms in an excited state was done by Wiberg and coworkers,<sup>48</sup> who calculated the values of the covalent bond order,<sup>49</sup> for a large set of singlet excited states of ethylene at the CIS level of theory. The first extensive study on the behavior of DI in excited states was reported by Wang and coworkers, who calculated the values of DI for

a large set of molecules using the Fulton approach in terms of 1-RDM at the CIS and EOM-CCSD levels of theory.<sup>50</sup> Recently, the DI values of the low-lying excited states have also been calculated in the framework of TDDFT for an iron complex.<sup>51</sup> However, in these studies the performance of Fulton and Ángyán indices has not been compared to the exact value of the DI for excited states and, consequently, it is not known which index performs better in excited states. To this end, the first part of this section is devoted to the study of the DI in the ground and low-lying singlet excited states of some small organic compounds. The information gathered in this section will shed some light on the suitability of the above mentioned approximations to compute the values of PDI, FLU,  $I_{\text{ring}}$ , and MCI descriptors of aromaticity in the excited states.

Table 1 presents the values of DIs obtained using the exact 2-RDM ( $\delta^{\text{act}}(A,B)$ ), Fulton ( $\delta^{\text{F}}(A,B)$ ), and Ángyán ( $\delta^{\text{A}}(A,B)$ ) indices for the ground singlet state and three of the lowest-lying singlet states of  $\text{C}_2\text{H}_4$  at the CASSCF level of theory. The active space chosen for this molecule contains 4 electrons and 4 orbitals corresponding to the pairs of  $\sigma/\sigma^*$  and  $\pi/\pi^*$  C–C bonding and antibonding orbitals. The configuration of the ground state is  $\sigma^2 \pi^2$ . To study the changes on DIs, we have selected three excited states: first, we study the excitation of one-electron from  $\pi$  to  $\pi^*$ , i.e.  $\sigma^2 \pi^1 \pi^{*1}$ ; second, we analyze the electronic consequences of exciting one electron from a  $\sigma$  to a  $\pi^*$  orbital; finally, the comparison between different DIs is completed with the double excitation from  $\pi$  to  $\pi^*$ . In all cases, the geometry of the system corresponds to the one obtained in the ground state and, thus, we only relax the molecular orbitals of the desired excited state (vertical excited state). To compare the values of  $\delta(A,B)$  with the **single determinant** ESI, we have calculated ESI values in the singlet ground state using B3LYP at the CASSCF optimized geometry (**HF results can be found in Table S1 of the Supporting Information**). As was previously observed at the CISD level,<sup>20c</sup> the CASSCF

value of  $\delta^{\text{xct}}(\text{C,C})$  in the ground state is significantly lower in comparison with the one obtained at the B3LYP level, 1.349 e and 1.900 e respectively. This is the result of including Coulomb correlation in the calculation of the  $\delta^{\text{xct}}(\text{C,C})$  value. On the other hand,  $\delta^{\text{F}}(\text{C,C})$  and  $\delta^{\text{A}}(\text{C,C})$  values are higher than  $\delta^{\text{xct}}(\text{C,C})$  but lower than  $\delta^{\text{B3LYP}}(\text{C,C})$ ,  $\delta^{\text{F}}(\text{C,C})$  being the one that better reflects the effect of correlation in the ESI. This observation can be associated with the fact that  $\delta^{\text{A}}(\text{C,C})$  only includes the exchange correlation. It is worth noticing that  $\delta^{\text{F}}(\text{C,C})$  value of 1.466 e obtained at the CASSCF level (see Table 1) is in line with the 1.491 e obtained by Wang and coworkers at the CCSD level.<sup>50</sup>

Table 1, here

Let us now analyze the performance of the above-mentioned indices to assess the degree of electron delocalization in some low-lying vertical excited states. First, we focus our attention on the excitation from the bonding  $\pi$  to the antibonding  $\pi^*$  orbital. Since an antibonding orbital is populated, a reduction of DI values in comparison with the ground state is expected. This trend is reproduced by the three indices,  $\delta^{\text{xct}}(\text{C,C})$ ,  $\delta^{\text{F}}(\text{C,C})$ , and  $\delta^{\text{A}}(\text{C,C})$ , that show values of 1.046 e, 1.078 e, and 1.084 e, respectively. The small differences among DIs might be related to the lower Coulomb correlation present in the vertical  $\pi \rightarrow \pi^*$  excited state. The value of  $\delta^{\text{F}}(\text{C,C})$  presented in Table 1 is comparable to the 1.233 e and 1.166 e, that were obtained at the CIS and EOM-CCSD levels of theory by Wang and coworkers for the first vertical excited state of ethylene.<sup>50</sup> Second, we analyze the excitation of one electron from the bonding  $\sigma$  to the antibonding  $\pi^*$  orbital. In this case, we also expect a decrease of electron delocalization between the carbon atoms with respect to the ground state because an antibonding orbital is

populated. Interestingly,  $\delta^F(C,C)$ , and  $\delta^A(C,C)$  show an abrupt reduction while the exact value predicts a smaller decrease. To analyze this behavior, we have separated the value of  $\delta^{xct}(C,C)$  into its  $\delta^{\sigma\sigma}(C,C)$  and  $\delta^{\sigma\sigma'}(C,C)$  terms (where  $\sigma = \alpha$  or  $\beta$ ). In the ground state the CASSCF values of  $\delta^{\sigma\sigma}(C,C)$  and  $\delta^{\sigma\sigma'}(C,C)$  are 1.825 e and -0.476 e respectively. As shown in Table 1,  $\delta^{\sigma\sigma}(C,C)$  and  $\delta^{B3LYP}(C,C)$  are practically the same, the inclusion of Coulomb correlation leads to a reduction of almost 0.5 e to the total DI. The splitting of  $\delta^{xct}(C,C)$  in the  $\sigma \rightarrow \pi^*$  singlet vertical excited state produces values of 1.244 e and 0.022 e for  $\delta^{\sigma\sigma}(C,C)$  and  $\delta^{\sigma\sigma'}(C,C)$  terms. It is interesting to note that  $\delta^{\sigma\sigma}(C,C)$  is significantly reduced with respect to the ground state because there are two  $\pi$ -electrons (out of the total three) of the same spin occupying  $\pi$  and  $\pi^*$  orbitals. On the contrary,  $\delta^{\sigma\sigma'}(C,C)$  contribution is almost zero due to the reduction of the Coulomb correlation in the excitation of one of the two electrons of the  $\sigma$  to the  $\pi^*$  orbital. The analysis of the natural orbital occupancies shows values of 1.997 e for the bonding  $\pi$  orbital and values of 0.997 e and 1.003 for  $\sigma$  and  $\pi^*$  orbitals, describing a practically **single determinant** unrestricted (UHF) situation. According to  $\delta^{xct}(C,C)$ , the double excitation from  $\pi$  to  $\pi^*$  orbitals leads to an increase of electron delocalization between the carbon atoms. This result may be explained by the fact that the calculation is performed at the ground state geometry, and because the  $\delta^{\sigma\sigma'}(C,C)$  term is less significant in comparison with the ground state, 0.052 e and 0.476 e, respectively. Finally, the values of  $\delta^F(C,C)$  and  $\delta^A(C,C)$  for the double excitation are considerably larger than the above-mentioned  $\pi \rightarrow \pi^*$  and  $\sigma \rightarrow \pi^*$  excited states but they are still lower than the value obtained in the ground state. In this case is the  $\delta^A(C,C)$  the one closer to the exact value.

In addition, we have studied the ground and some low-lying singlet states of  $C_2H_2$  and  $CH_2O$ . Table 1 compares the values of DI for the ground state of  $C_2H_2$  obtained at the CASSCF and B3LYP levels (**HF results can be found in Table S1 of the**

**Supporting Information**). The active space of  $C_2H_2$  contains six electrons in six orbitals, i.e. C–C bonding and antibonding  $\sigma/\sigma^*$  pair, and the in-plane and out-of-plane  $\pi/\pi^*$  degenerate orbitals. The values of  $\delta(C,C)$ ,  $\delta^F(C,C)$ , and  $\delta^A(C,C)$  are larger than the previously observed DI for  $C_2H_4$ . Once more,  $\delta^F(C,C)$  and  $\delta^A(C,C)$  are higher than the exact value, being the Fulton index the one that approaches better  $\delta^{xct}(C,C)$ . We have selected two excited states, the first one is a single electron excitation which is a mixture of two configurations that present the same weight, the excitation from  $\pi_{in}$  to  $\pi_{in}^*$  and from  $\pi_{out}$  to  $\pi_{out}^*$ ; second, we have considered a two-electron excitation, one electron goes from  $\pi_{in}$  to  $\pi_{in}^*$  and the other from  $\pi_{out}$  to  $\pi_{out}^*$ . All DIs calculated at both excited states predict a reduction of electron delocalization between carbon atoms in comparison with the ground state, although the double-excitation leads to an abrupt decrease as expected from the fact that the two  $\pi$ -bonds are broken simultaneously. Finally, the ground and low-lying excited states of formaldehyde have been studied. The active space chosen for this molecule is made of 6 electrons and 5 orbitals that consist of the C=O bonding and antibonding pairs of the  $\sigma/\sigma^*$  and  $\pi/\pi^*$  orbitals, and one of the n orbitals corresponding to an oxygen lone pair. In this case, we have analyzed four singlet excited states, i.e. three monoexcitations,  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$ , and  $\sigma \rightarrow \pi^*$ , and two double excitations, the excitation of two electrons from  $\pi \rightarrow \pi^*$  and the simultaneous one-electron transition from  $\sigma$  and  $\pi$  to  $\pi^*$  (see Table 1). All single excitations analyzed in the present work populate the  $\pi^*$  orbital and, thus, we observe a decrease of the electron delocalization between the carbon and oxygen atoms. However, both  $\pi \rightarrow \pi^*$  and  $\sigma \rightarrow \pi^*$  transitions show a large decrease of electron sharing because a bonding orbital is depopulated, while  $\delta^{xct}(C,C)$ ,  $\delta^F(C,C)$  and  $\delta^A(C,C)$  values associated with the  $n \rightarrow \pi^*$  transition are less affected by the excitation due to the fact that the excited electron goes from a lone pair orbital to an antibonding orbital. As previously

seen for ethylene, the double excitation of two-electrons from  $\pi$  to  $\pi^*$  orbitals leads to an enhancement of electron delocalization in comparison with the excited states characterized by single excitations (see Table 1). When the double excitation takes place from two different orbitals, i.e.  $\sigma$  to  $\pi$ , the values of  $\delta^{\text{xc}}(\text{C,C})$ ,  $\delta^{\text{F}}(\text{C,C})$ , and  $\delta^{\text{A}}(\text{C,C})$  are lower than in the previous case.

One of the advantages of DI analysis is that it reflects the effect of the excitation in the bonds without the need of optimizing the geometry of the excited state. Our results suggest that the Fulton index is the approximation to the ESI that performs better to evaluate electron delocalization in the ground state at the CASSCF level of theory. Interestingly, both indices perform similarly in the excited states and provide better results in the excited states than in the ground state. In the case of single excitations, we have observed a decrease of electron sharing. When the two electrons of the double-excitation go to the same orbital, DIs are less affected with respect to the ground state if geometry relaxation is not allowed. In the following section we will analyze the ability of electron delocalization measures to predict the aromaticity of singlet, triplet, quintet, and septet excited states.

## **B. Electron delocalization and aromaticity in the ground and low-lying excited states of benzene**

Aromaticity is a concept that has been widely discussed for a large series of ground state molecules. Several descriptors and simple rules have been put forward to account for the degree of aromaticity of a huge variety of species. However, as it is pointed out in the introduction of this work, less attention has been paid to elucidate the nature of aromaticity and antiaromaticity in low-lying excited states. The work of Baird signified a breakthrough towards the understanding of triplet state aromaticity.<sup>4</sup> The



existence of aromaticity in the lowest-lying triplet state has been corroborated by means of various indices of aromaticity for a large list of annulenes with  $4n\pi$ -electrons.<sup>9b, 10, 52</sup> Since multireference wavefunctions are needed to describe the electronic structure of excited states, the assessment of aromaticity in such states has been limited to the analysis of structural parameters. One of the first attempts to describe the aromaticity of excited states using aromaticity indices based on magnetic properties was done by Karadakov, who used NICS, proton shielding, and magnetic susceptibilities to discuss the aromaticity of the lowest-lying singlet and triplet states of  $C_6H_6$ ,  $C_4H_4$ , and  $C_8H_8$ .<sup>15</sup> To broaden the scope of the aromaticity analysis in excited states, we aim to extend the use of electronic aromaticity indices such as PDI, FLU,  $I_{ring}$ , and MCI to assess the aromatic character of some low-lying excited states.

First, we start with the electronic delocalization analysis of aromatic molecules focusing our attention on the benzene molecule. To describe the electronic structure of  $C_6H_6$ , we have carried out CASSCF calculations with an active space that contains six electrons in six orbitals, which correspond to the three pairs of  $\pi/\pi^*$  bonding and antibonding orbitals (see Figure 1). Thus, the excited states studied in this work only present excitations between  $\pi$  orbitals. Table 2 shows the configurations and excitations with respect to the ground state for the vertical singlet, triplet, and quintet excited states analyzed. In addition, the vertical excitation energies of these singlet, triplet, and quintet states are provided. The values obtained for  $S_1$  and  $T_1$  agree very well with the results presented by Karadakov which were compared with experimental data and more refined theoretical calculations.<sup>15a</sup> In Figure 2, the values of  $\delta^F(C,C)$  between adjacent carbon atoms are depicted in order to analyze the effect of excitation on the electron distribution. As shown in Figure 2, the values of DIs calculated at the excited states do not depend on the symmetry of the ground state ( $D_{6h}$  in  $C_6H_6$ ). Thus, DIs can reveal the

nature of the excited state without reoptimizing the geometry of the excited state. Moreover, Table 2 provides the values of PDI and FLU indices obtained using both Fulton and Ángyán indices while  $I_{\text{ring}}$  and MCI are computed using Eqs. (11) and (12), respectively. Since PDI and FLU values give the same trends for Fulton and Ángyán indices (see Tables 2, 4, and 5), we focus our attention on the results given by the Fulton approximation.

Tables 2 and 3 and Figures 1 and 2, here

Let us now first study the values obtained for the ground state of benzene. Figure 2 shows that all  $\delta^{\text{F}}(\text{C,C})$  are 1.288 e, reproducing the  $D_{6h}$  symmetry of the ground state of  $\text{C}_6\text{H}_6$ . These values are similar to the 1.230 e obtained by some of us using the Fulton index at the CISD level of theory.<sup>20c</sup> The strong electron delocalization through the carbon atoms typical of  $\text{C}_6\text{H}_6$  is responsible for the high value of  $\text{PDI}^{\text{F}}$ , which measures the number of electrons delocalized between the carbons in para-position of the 6-MR. The effect of electron correlation significantly reduces the value of the PDI, 0.103 e at the B3LYP (see Table 3; for HF values see Table S2 of the Supporting Information) to 0.050 e at the CASSCF level. Since benzene is the reference value for the  $\text{C}\square\text{C}$  delocalization index used in FLU,  $\text{FLU}^{\text{F}}$  is zero for the ground state. A reduction of  $I_{\text{ring}}$  and MCI values is also observed with respect to **single determinant** methods (see Tables 2 and 3). As was previously noticed for simple organic compounds, the inclusion of electron correlation leads to a notable decrease of electron sharing in aromatic molecules.

Next, we analyze the performance of the above mentioned electronic aromaticity indices to predict the degree of aromaticity in some of the low-lying singlet states. The

first excited state is basically represented by two configurations with the same weight that are defined by the excitations from the bonding  $\pi_2$  to the antibonding  $\pi_4^*$  and from  $\pi_3$  to  $\pi_5^*$ . Interestingly, the values of  $\delta^F(\text{C,C})$  show that the  $D_{6h}$  symmetry of the ground state is kept in the  $S_1$ , although the electron sharing between adjacent carbons is significantly reduced, i.e. 1.288 e in  $S_0$  and 1.189 e in  $S_1$  (see Figure 2). Thus, the population of antibonding  $\pi_4^*$  and  $\pi_5^*$  orbitals causes a reduction of electron delocalization with respect to the ground state. According to the DI, a decrease of aromaticity is expected when going from  $S_0$  to  $S_1$ . All analyzed indices reproduce this trend, namely,  $\text{PDI}^F$  goes from 0.05 e to 0.01 e, while  $I_{\text{ring}}$  and MCI values are almost zero for  $S_1$ , except FLU that increases only slightly from 0.000 to 0.006 (see Table 2). With the exception of FLU, the electronic aromaticity indices indicate that the  $S_1$  of benzene can be classified as antiaromatic. These results are in agreement with previous NICS and magnetic susceptibilities values that predicted an antiaromatic character for the first excited state of benzene.<sup>15a</sup> In addition, we have studied the aromaticity of degenerate  $S_2$  and  $S_3$  vertical excited states of  $\text{C}_6\text{H}_6$ . Despite they present the same vertical excitation energy, the electronic distribution is considerably different. Both states are a mixture of different contributions with important weights. In summary,  $S_2$  is dominated by the excitation of one electron to  $\pi_4^*$ , while in  $S_3$  it is the antibonding  $\pi_5^*$  orbital that is populated the most. The nature of the excitation is translated to the DI values. As the symmetry of the antibonding orbitals which are populated, the picture provided by the  $\delta^F(\text{C,C})$  values exhibits a  $D_{2h}$  symmetry (see Figure 2). However, in  $S_2$  there are four values of  $\delta^F(\text{C,C})$  which are 1.203 e while the remaining two have 1.092 e. Thus, the electrons are delocalized among two groups of three carbons (see Figure 2). On the other hand,  $\delta^F(\text{C,C})$  of  $S_3$  shows that the electrons are basically shared between two bonds, while the remaining four present single bond character. The distortion on the

electronic distribution with respect to the ground state symmetry predicted by the DI should lead to a loss of aromaticity larger than in  $S_1$ . As shown in Table 2,  $\text{PDI}^F$ ,  $\text{FLU}^F$ ,  $I_{\text{ring}}$ , and MCI values are practically the same for  $S_2$  and  $S_3$  and point out a lower aromaticity in comparison to the  $S_0$  ground state.  $\text{FLU}^F$ ,  $I_{\text{ring}}$ , and MCI indicate that  $S_2$  and  $S_3$  are more antiaromatic than  $S_1$ , while  $\text{PDI}^F$  predicts the opposite trend. This is likely a failure of the PDI measure that also breaks down by slightly overestimating the degree of aromaticity in some benzene distortions such as the boat or chair-like deformations.<sup>31b, 53</sup> Until now, we have analyzed singlet-excited states that are represented by a mixture of single excitations. Next, we focus our attention on the double excitation from one-electron of  $\pi_2$  to  $\pi_4^*$  and another from  $\pi_3$  to  $\pi_5^*$  which corresponds to the seventh-excited state of benzene calculated at the SA-CASSCF(6,6)/6-311++g(d,p) level of theory. As it is shown in Figure 2, the  $\delta^F(\text{C,C})$  values resulting from the double excitation keep the  $D_{6h}$  symmetry of the ground state but are lower than the ones found in  $S_0$  and  $S_1$ .  $I_{\text{ring}}$  and MCI show the antiaromatic character of  $S_7$ , while  $\text{PDI}^F$  values, which are three times larger than in  $S_1$  (see Table 2), and  $\text{FLU}^F$  results are less conclusive about the antiaromatic character of  $S_7$ . Overall, we found that the low-lying singlet states of benzene are antiaromatic.

To study the consequences of  $4n\pi$ -electrons triplet state aromaticity, we have analyzed the electron delocalization on the lowest-lying triplet excited states of  $\text{C}_6\text{H}_6$ . In  $T_1$ , the unpaired electrons are localized in the  $\pi_2$  and  $\pi_5^*$  orbitals. According to the work of Baird, the lowest-lying triplet state,  $T_1$ , of benzene should be antiaromatic.<sup>4</sup> The results presented in Table 2 agree very well with this statement,  $\text{PDI}^F$  is 0.015 e,  $\text{FLU}^F$  takes values of 0.020, and  $I_{\text{ring}}$  and MCI are practically zero. These results are in agreement with NICS values reported by Karadakov that predict a strong paratropic ring current for  $T_1$ .<sup>15a</sup> In addition, the values of  $\delta^F(\text{C,C})$  predict a strong reduction of

symmetry in comparison with  $S_0$ , with two values equal to 1.429 e while the remaining four are 1.100 e. The same trends are observed for the  $T_2$ ,  $T_3$ , and  $T_4$  states. In all cases, the loss of symmetry exhibited by  $\delta^F(C,C)$  is less pronounced than in  $T_1$ . The values of  $PDI^F$ ,  $FLU^F$ ,  $I_{ring}$ , and MCI predict an antiaromatic character for the lowest-lying triplet states of benzene (see Table 2).

In 2008, Soncini and Fowler proposed to extend Baird's rule to take into account higher order multiplicities such as quintets or septets.<sup>18</sup> They found that compounds with  $(4n+2)\pi$ -electrons which are aromatic in their lowest-lying singlet state should be aromatic in the lowest-lying quintet state, and antiaromatic in the lowest-lying triplet state but also in the lowest-lying septet state. On the contrary, systems with  $4n\pi$ -electrons are antiaromatic in their lowest-lying singlet and quintet states whereas they are aromatic in the lowest-lying triplet and septet states. To study the consequences of this generalization, we have performed the analysis of electron delocalization on the three lowest-lying quintet vertical excited states of benzene. In the lowest-lying first quintet excited state, the unpaired electrons are basically localized in  $\pi_2$ ,  $\pi_3$ ,  $\pi_4^*$ , and  $\pi_5^*$  orbitals, although there is also a significant correlation between  $\pi_1$  and  $\pi_6^*$  orbitals. Interestingly, the picture of the electronic distribution provided by the values of DI keeps the  $D_{6h}$  symmetry of the singlet ground state (see Figure 2). The value of MCI obtained at the B3LYP level for the lowest-lying quintet state is 0.045 e (see Table 3), slightly smaller than the value of benzene, 0.072 e. Apparently, this result confirms the validity of the extended rule proposed by Soncini and Fowler. However, at the correlated level of theory, the value of MCI for the  $Q_1$  state is extremely reduced with respect to the one obtained at the B3LYP level of theory, 0.002 in the former while 0.045 in the latter (see Tables 2 and 3).  $PDI^F$  also shows an important reduction in comparison with the values obtained at the B3LYP level of theory (see Tables 2 and 3).

Thus, the values of electronic delocalization and multicenter indices are significantly affected by the inclusion of electron correlation. As a whole, our results do not support the validity of Soncini and Fowler's generalization of Baird's rule to the lowest-lying quintet state of  $(4n+2)\pi$ -electron systems. In  $Q_2$  and  $Q_3$  degenerate states, the values of  $\delta^F(C,C)$  show a non-symmetric distribution of electrons. Thus, the values of electronic aromaticity indices are lower than in  $Q_1$ . The following section is devoted to the analysis of aromaticity in compounds that are antiaromatic in their respective singlet ground states.

### **C. Electron delocalization and aromaticity in the ground and low-lying excited states of antiaromatic systems: cyclobutadiene and cyclooctatetraene**

To assess the aromaticity of low-lying singlet and triplet states of antiaromatic compounds, we have selected the archetypical  $C_4H_4$  and  $C_8H_8$  systems. According to the  $(4n+2)\pi$ -electron rule proposed by Hückel, molecules with  $4n\pi$ -electrons are antiaromatic in the singlet ground state. First, we focus our attention on the  $D_{2h}$   $C_4H_4$  molecule. The active space is made of four electrons and four  $\pi$  orbitals (see Figure 1). The electronic distribution of each vertical excited state in terms of  $\delta^F(C,C)$  is depicted in Figure 3 and the values of electronic aromaticity indices are summarized in Table 4. The values of  $\delta^F(C,C)$  reproduce the  $D_{2h}$  symmetry of the ground state, two bonds have 1.480 e and, thus, present double bond character while the other two have 1.002 e typical of a single bond. The significant difference between  $\delta^F(C,C)$  values is characteristic of antiaromatic compounds. In contrast to  $S_0$  of benzene, the ground state of cyclobutadiene presents large  $FLU^F$  values, i.e. 0.036 in the latter. The antiaromaticity of  $S_0$  is also confirmed by electronic multicenter indices, namely,  $I_{ring}$  and MCI that show values close to zero, 0.006 and 0.009 respectively. Let us now

analyze the aromaticity of the three lowest-lying singlet states of  $C_4H_4$ . The first singlet-excited state,  $S_1$ , is basically characterized by the double excitation from  $\pi_2$  to the  $\pi_3^*$  orbital. The  $\pi_2$  and  $\pi_3^*$  orbitals are affected by the Jahn-Teller distortion, that leads to a geometry distortion from  $D_{4h}$  to  $D_{2h}$  of the  $C_4H_4$  ground state. In the  $D_{2h}$  symmetry, both orbitals have similar shapes (see Figure 1) and are almost degenerate. Thus, the double excitation between these orbitals results in an excited state that shows some similarities with  $S_0$ . As can be seen from Figure 3, the picture of the electron distribution described by  $\delta^F(C,C)$  values is reversed for  $S_1$ . In contrast to  $S_0$ , the bonds  $C_1-C_2$  and  $C_3-C_4$  exhibit a higher degree of electron delocalization than  $C_1-C_4$  and  $C_2-C_3$  because the  $\pi_3^*$  orbital is populated (labels of atoms are given in Table 4). Despite the double excitation, the  $\pi_2$  orbital remains partially populated in  $S_1$  (the occupation number of  $\pi_2$  is equal to 0.322 e) and, consequently, the difference between double and single bonds is less pronounced, i.e. 1.278 vs 1.101 e. These results may be explained by the fact that we are studying the vertical excited states obtained from the  $D_{2h}$  geometry, which is defined by  $\pi_1$  and  $\pi_2$  orbitals while  $S_1$  forces a  $D_{2h}$  geometry characterized by  $\pi_1$  and  $\pi_3^*$  orbitals. In the last five years, theoretical studies have shown that  $S_1$  is unstable in its rectangular form.<sup>54</sup> This instability is reproduced by  $I_{ring}$  and MCI, which assign a clear antiaromatic character to  $S_1$ , similar to the one found in  $S_0$  (see Table 4). The same conclusions has been obtained by means of NICS calculations.<sup>15a</sup> On the other hand, the value of  $FLU^F$  is three times lower than in  $S_0$  because the difference between  $\delta^F(C,C)$  has been reduced. In this case, the value of  $FLU^F$  overestimates the aromaticity of the first excited state with respect to the ground state. These failures of FLU can be attributed to the reference values used to construct this index. This is reminiscent of the failure of FLU to identify the transition state of Diels-Alder reaction as aromatic.<sup>31a</sup> FLU

measures resemblance with C=C bond in benzene; if the molecule is aromatic but it does not have similar C=C bonding to benzene FLU will not identify it as aromatic.

Figure 3 and Table 4, here

The second vertical excited state,  $S_2$ , is represented by the excitation of one electron from  $\pi_2$  to  $\pi_3^*$  orbitals. This excitation leads to a more delocalized situation, represented by the tendency to the equalization of  $\delta^F(C,C)$  values which are 1.290 e and 1.190 e. Interestingly, the  $I_{ring}$  and MCI values for  $S_2$  are 0.045 and 0.049 respectively, similar to those obtained for the ground state of benzene (see Tables 2 and 3). Consequently, the  $S_2$  state of  $C_4H_4$  can be classified as aromatic according to electronic multicenter indices of aromaticity. This observation is supported by the  $FLU^F$  value, which is almost zero. Remarkably, NICS values classify this state as nonaromatic or slightly antiaromatic.<sup>15a</sup> To solve this controversy, we have optimized the minimum of  $S_2$  represented by the configuration of  $\pi_1^2\pi_2^1\pi_3^{*1}$ . The optimization rapidly leads to a  $D_{4h}$  minimum where all C=C bond lengths are 1.422 Å. At this stationary point, the values of  $FLU^F$ ,  $I_{ring}$ , and MCI are 0.001, 0.045, and 0.049. As shown in Table 4, no significant differences are observed in comparison with  $S_2$  values obtained from the vertical excitation of the  $D_{2h}$  ground state geometry. Thus, electronic aromaticity indices reflect the aromaticity of the excited state without the need of reoptimizing the geometry of the vertical excitation, while NICS values are more affected by the geometry of the system.<sup>15a</sup> Finally, we have studied the third singlet-excited state,  $S_3$ , which is dominated by one-electron excitations from  $\pi_2$  to  $\pi_4^*$  but the contribution of the excitation from  $\pi_1$  to  $\pi_3^*$  is non-negligible. Since both one-electron excitations represented by their corresponding configuration state functions do not present the same weight, a non-



symmetrical picture of  $\delta^F(\text{C,C})$  is expected. The DI show a rectangular distribution with values of 1.249 and 1.026 e. The large alternation exhibited by  $\delta^F(\text{C,C})$  can be related to the antiaromaticity of  $S_3$ . These results are confirmed by a large value of  $\text{FLU}^F$ , and low values of  $I_{\text{ring}}$  and MCI. In summary, according to electron multicenter indices, the vertical  $S_0$ ,  $S_1$ , and  $S_3$  states of  $\text{C}_4\text{H}_4$  are antiaromatic while  $S_2$  is clearly aromatic. However, it is likely that this  $S_2$  state becomes  $S_1$  if one performs a geometry optimization of the different excited states.

Next, we focus our attention on the low-lying triplet states of  $\text{C}_4\text{H}_4$ . To calculate the values of the  $\delta^F(\text{C,C})$ ,  $\text{FLU}^F$ ,  $I_{\text{ring}}$ , and MCI, the  $D_{2h}$  geometry of the  $S_0$  ground state has been used (see Table 4). The first triplet state,  $T_1$ , presents the following configuration: two electrons in  $\pi_1$ , and one in  $\pi_2$  and  $\pi_3^*$ . The analysis of DIs show that there is a tendency towards the equalization of  $\delta^F(\text{C,C})$  with respect to the singlet ground state. This observation clearly anticipates the aromatic character of the  $T_1$  state, which is confirmed by  $\text{FLU}^F$ ,  $I_{\text{ring}}$ , and MCI values of 0.009, 0.033, and 0.036. As was shown by Baird, the lowest-lying triplet state of systems with  $4n\pi$ -electrons is aromatic. These results are in agreement with NICS(0), NICS(1), and NICS(1)<sub>zz</sub> calculations reported by Karadakov for the  $D_{2h}$   $T_1$  state.<sup>15a</sup> On the contrary, the z-component of NICS(0), i.e. NICS(0)<sub>zz</sub>, takes positive values, indicating that  $T_1$  is antiaromatic. In order to analyze the effect of geometry relaxation on electronic aromaticity indices, we have optimized the  $T_1$  minimum. As expected, the most stable structure of the  $T_1$  state is a square with  $D_{4h}$  symmetry.<sup>54b, 54c</sup> As has been previously observed for the  $S_2$  state of  $\text{C}_4\text{H}_4$ , the values of electronic aromaticity indices in the optimized  $T_1$  state are practically the same, namely,  $\text{FLU}^F$ ,  $I_{\text{ring}}$ , and MCI are 0.007, 0.034, and 0.036 respectively. Again, the inclusion of electron correlation leads to a significant decrease of MCI with respect to B3LYP value, which is 0.127 e (see Tables 3 and 4). Since the aromatic character of

more energetic triplet excitations has not been studied yet, we performed the aromaticity analysis of  $T_2$ ,  $T_3$ , and  $T_4$  states of  $C_4H_4$ . The configuration of these states can be found in Table 4. The values of DI obtained for  $T_2$ ,  $T_3$ , and  $T_4$  indicate a reduction of electron delocalization between carbon atoms with respect to  $T_1$  (see Figure 3). The global decrease of electron sharing depicted by DI is translated into the values of aromaticity indices, which assign a clear antiaromatic character to  $T_2$ ,  $T_3$ , and  $T_4$  states (see Table 4). Overall,  $T_1$  can be classified as aromatic whereas the remaining  $T_2$ ,  $T_3$ , and  $T_4$  states present antiaromatic character.

Finally, we study the aromaticity and antiaromaticity patterns of the low-lying singlet, triplet, quintuplet, and septet states of the planar  $C_8H_8$  (note that this structure is not the energy minima, which is a non-aromatic non-planar species). To characterize the electronic structure of this molecule by means of CASSCF calculations, an active space with eight electrons and eight  $\pi$  orbitals has been selected (see Figure 1). Consequently, the excited states analyzed in this work only take into account  $\pi \rightarrow \pi^*$  transitions (see Table 5). The vertical excitations have been performed at the  $D_{4h}$  geometry of  $C_8H_8$ . The electron distribution provided by the values of  $\delta^F(C,C)$  is depicted in Figure 4 and the values of electronic aromaticity indices are collected in Table 5. According to the  $4n+2$  electron rule, the singlet ground state of  $C_8H_8$  is classified as antiaromatic because it has eight  $\pi$  electrons. The antiaromaticity of  $C_8H_8$  with  $D_{4h}$  symmetry has been widely discussed. In particular, from the structural point of view this compound presents a clear bond length alternation typical of antiaromatic systems. The observed bond length alternation is preserved in the picture of the electron distribution provided by the DI. The electrons are mainly delocalized between the carbon atoms that form the four double C=C bonds,  $\delta^F(C,C)$  is 1.482 e, while only 1.083 e are delocalized in the four remaining single C-C bonds. At the B3LYP level of theory, these values are 1.715 and

1.084 e. Thus, the inclusion of electron correlation leads to a significant reduction of electron sharing between the carbon atoms that form the double bond. The value of  $FLU^F$  is 0.024, which is significantly larger with respect to the value of benzene, indicating the antiaromatic character of this compound. This observation is confirmed by  $I_{ring}$  and MCI indices that are almost zero in the  $S_0$  state of  $C_8H_8$ , i.e. 0.0011 and 0.0005 e, respectively. These results are in agreement with previous NICS calculations that indicate the presence of a strong paratropic ring current in the ground state of  $C_8H_8$ .<sup>15b, 55</sup> As previously observed for  $C_4H_4$ , the first excited state of  $C_8H_8$ ,  $S_1$ , is characterized by the double excitation from  $\pi_4$  to  $\pi_5^*$  orbitals. As shown in Figure 4, the excitation of two electrons causes the inversion of  $\delta^F(C,C)$  with respect to the ground state. Since the  $\pi_4$  and  $\pi_5^*$  orbitals are quite similar, the double excitation between these orbitals preserve the antiaromaticity of the system. This trend is reproduced by the electronic multicenter indices, which are practically zero (see Table 5). On the other hand, the second vertical excited state,  $S_2$ , is represented by the one-electron excitation from  $\pi_4$  to  $\pi_5^*$ . This excitation gives rise to an equalization of  $\delta^F(C,C)$  and, therefore, we expect an increase of aromaticity. In comparison with  $S_0$ ,  $FLU^F$  exhibits a clear reduction of its values, from 0.024 to 0.002, pointing out the aromatic character of  $S_2$ .  $I_{ring}$  and MCI also indicate an increase of aromaticity. For instance, MCI value is twelve times larger in  $S_2$  than in  $S_0$ , 0.0061 vs. 0.0005. Again, it is likely that this  $S_2$  vertical excited state becomes  $S_1$  after geometry optimization. Next, we focus on the third singlet excited state,  $S_3$ , which is a mixture of excitations from  $\pi_2$ ,  $\pi_3$ , and  $\pi_4$  to  $\pi_5^*$  orbitals that cause an asymmetric electron distribution of the DIs (see Figure 4). The values of  $\delta^F(C,C)$  are considerably lower than in the previous excited states, pointing out the antiaromaticity of  $S_3$  which is confirmed by the values of electronic aromaticity indices (see Table 5).

Figure 4 and Table 5, here

In contrast to  $S_0$ , the lowest-lying triplet state of  $C_8H_8$  is aromatic according to Baird's rule. The aromaticity of  $T_1$  has been corroborated by means of magnetic indices of aromaticity<sup>9b, 15b</sup> and electronic delocalization measures.<sup>52</sup> As previously seen for  $S_2$ , the lowest-lying triplet state shows a tendency towards DI equalization with respect to  $S_0$  (see Figure 4). The values of  $FLU^F$ ,  $I_{ring}$ , and MCI are 0.003, 0.0033 and 0.0047 (see Table 5) respectively, similar to those obtained for the  $S_2$  state. Therefore, the  $T_1$  state can be classified as aromatic in agreement with Baird's rule and previous NICS calculations. Interestingly, the value of MCI calculated at the B3LYP level of theory is 0.0271 (see Table 3), indicating that it is significantly reduced by the inclusion of electron correlation. On the contrary, degenerate  $T_2$  and  $T_3$  vertical states show an alternated electron distribution that leads to high values of  $FLU^F$  and low values of  $I_{ring}$  and MCI (see Figure 4 and Table 5) indicating a clear antiaromatic character. In summary,  $S_2$  and  $T_1$  vertical states of  $C_8H_8$  can be considered aromatic while  $S_0$ ,  $S_1$ ,  $S_3$ ,  $T_2$ , and  $T_3$  can be classified as antiaromatic.

To study the generalization of Baird's rule proposed by Soncini and Fowler,<sup>18</sup> we have calculated the electron delocalization indices in the lowest-lying quintet and septet vertical states of  $D_{4h}$   $C_8H_8$  (see Figure 4 and Table 5). According to this generalized rule, the lowest-lying quintet state of  $4n\pi$ -electron systems is antiaromatic while the lowest-lying septet state can be considered aromatic. The first quintet state calculated as vertical excitation from the  $D_{4h}$  ground state geometry is a mixture of two configurations with the same weight, one with the unpaired electrons localized in orbitals  $\pi_3$ ,  $\pi_4$ ,  $\pi_5^*$ , and  $\pi_6^*$  whereas in the other configuration the unpaired electrons are

in  $\pi_2$ ,  $\pi_4$ ,  $\pi_5^*$ , and  $\pi_7^*$ . The electronic distribution depicted by DI show a  $D_{4h}$  symmetry with an alternation between the values of  $\delta^F(C,C)$ . As shown in Tables 3 and 5, the values of  $FLU^F$ ,  $I_{ring}$ , and MCI point out an antiaromatic character for the lowest-lying quintet state in both B3LYP and CASSCF levels of theory. These observations are in agreement with the generalization of Baird's rule proposed by Soncini and Fowler. On the other hand, the dominant configuration of the lowest-lying septet state localizes the unpaired electrons in orbitals  $\pi_2$ ,  $\pi_3$ ,  $\pi_4$ ,  $\pi_5^*$ ,  $\pi_6^*$ , and  $\pi_7^*$ . Interestingly, a strong correlation between  $\pi_1$  and  $\pi_8^*$  also exists (natural occupancies of 1.70 e and 0.30 e respectively). The electronic distribution provided by  $\delta^F(C,C)$  show a tendency toward DI equalization (see Figure 4). Notwithstanding, the values of  $\delta^F(C,C)$  are considerably reduced with respect to singlet and triplet states and present almost single bond character. At the B3LYP level of theory, the value of MCI is 0.0178, significantly larger than the one obtained for  $S_0$  and  $Q_1$ , and similar to the value of  $T_1$  (see Table 3). Thus, B3LYP calculations assign aromatic character to the lowest-lying septet state of  $C_8H_8$  in agreement with Soncini and Fowler expectations. However, when the effects of electron correlation are taken into account, this value is remarkably reduced to 0.0001 e and, therefore, our CASSCF results do not support the Soncini and Fowler generalization of Baird's rule. It is worth noting that Karadakov also observed a clear reduction of NICS when comparing the UHF and CASSCF values of the lowest-lying septet state.<sup>15b</sup>

## Conclusions

In the present work we have studied the electron delocalization and aromaticity of the ground state and several low-lying excited states in representative (anti)aromatic organic compounds such as benzene, cyclobutadiene, and cyclooctatetraene. This analysis is performed for the first time using multicenter electron delocalization indices

calculated from CASSCF wavefunctions. The results obtained convincingly show that benzene is aromatic in the ground state and cyclobutadiene and cyclooctatetraene are aromatic in their vertical  $S_2$  and  $T_1$  excited states. The aromaticity of the  $T_1$  state of these  $4n\pi$ -compounds is in line with the predictions from Baird's rule for triplet state aromaticity. Finally, our CASSCF results on the lowest-lying quintet state of benzene and septet state of cyclooctatetraene indicate that these states are not aromatic, and, therefore, do not support the Soncini and Fowler generalization of Baird's rule.

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## Supporting Information

Tables S1 with CASSCF, HF, and B3LYP DI values of  $C_2H_4$ ,  $C_2H_2$ ,  $CH_2O$  and Table S2 with PDI, FLU and multicenter indices of  $C_6H_6$ ,  $C_4H_4$ ,  $C_8H_8$  calculated at the HF/6-311++G(d,p) level of theory. This material is available free of charge via the internet at xxx.

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Table 1. CASSCF values of  $\delta^{\text{xct}}(A,B)$ ,  $\delta^{\text{F}}(A,B)$ , and  $\delta^{\text{A}}(A,B)$  for several low-lying singlet excited states of  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{CH}_2\text{O}$ . DI units are in electrons and bond distances in Å.

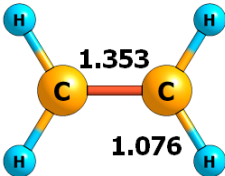
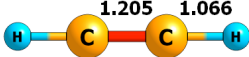
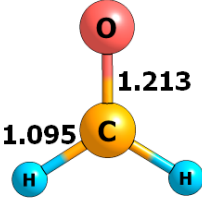
		Configuration	Excitation	$\delta^{\text{xct}}(A,B)$	$\delta^{\text{A}}(A,B)$	$\delta^{\text{F}}(A,B)$	$\delta^{\text{B3LYP}}(A,B)$
$\text{C}_2\text{H}_4$ $\delta(\text{C,C})$		$\sigma^2\pi^2$		1.349	1.732	1.466	1.900
		$\sigma^2\pi^1\pi^{*1}$	$\pi \rightarrow \pi^*$	1.046	1.084	1.078	
		$\sigma^1\pi^2\pi^{*1}$	$\sigma \rightarrow \pi^*$	1.248	1.007	1.041	
		$\sigma^2\pi^{*2}$	$\pi^2 \rightarrow \pi^{*2}$	1.519	1.589	1.324	
$\text{C}_2\text{H}_2$ $\delta(\text{C,C})$		$\sigma^2\pi_{\text{in}}^2\pi_{\text{out}}^2$		1.859	2.627	2.200	2.855
		$\sigma^2\pi_{\text{in}}^1\pi_{\text{out}}^2\pi_{\text{in}}^{*1}$	$\pi_{\text{in}} \rightarrow \pi_{\text{in}}^*$	1.579	1.536	1.422	
		$\sigma^2\pi_{\text{in}}^2\pi_{\text{out}}^1\pi_{\text{out}}^{*1}$	$\pi_{\text{out}} \rightarrow \pi_{\text{out}}^*$				
		$\sigma^2\pi_{\text{in}}^1\pi_{\text{out}}^1\pi_{\text{in}}^1\pi_{\text{out}}^1$	$\pi_{\text{in}}\pi_{\text{out}} \rightarrow \pi_{\text{in}}^*\pi_{\text{out}}^*$	1.295	1.127	1.240	
$\text{CH}_2\text{O}$ $\delta(\text{C,O})$		$\sigma^2\pi^2n^2$		1.243	1.420	1.314	1.583
		$\sigma^2\pi^2n^1\pi^{*1}$	$n \rightarrow \pi^*$	1.143	0.977	0.980	
		$\sigma^2\pi^1n^2\pi^{*1}$	$\pi \rightarrow \pi^*$	0.903	0.944	0.906	
		$\sigma^1\pi^2n^2\pi^{*1}$	$\sigma \rightarrow \pi^*$	0.994	0.786	0.860	
		$\sigma^2n^2\pi^{*2}$	$\pi^2 \rightarrow \pi^{*2}$	1.346	1.288	1.211	
		$\sigma^1\pi^1n^2\pi^{*2}$	$\sigma\pi \rightarrow \pi^{*2}$	1.213	1.117	1.021	

Table 2. Values of PDI, FLU,  $I_{\text{ring}}$ , and MCI for low-lying singlet, triplet, and quintet excited states of  $C_6H_6$ . Vertical excitation energies have been calculated with respect to the singlet ground state energy. All units are in au, except  $\Delta E(\text{eV})$  and bond distances which are in eV and  $\text{\AA}$ , respectively.

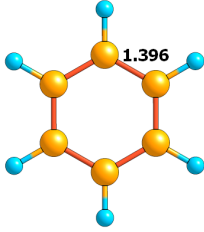
Singlet	State	Configuration	Excitation	PDI <sup>A</sup>	PDI <sup>F</sup>	FLU <sup>A</sup>	FLU <sup>F</sup>	$I_{\text{ring}}$	MCI	$\Delta E(\text{eV})$
 $C_6H_6$ $D_{6h}$	$S_0$	$\pi_1^2 \pi_2^2 \pi_3^2$		0.074	0.050	0.000	0.000	0.0305	0.0435	0.00
	$S_1$	$\pi_1^2 \pi_2^1 \pi_3^2 \pi_4^{*1}$ $\pi_1^2 \pi_2^2 \pi_3^1 \pi_5^{*1}$	$\pi_2 \rightarrow \pi_4^*$ $\pi_3 \rightarrow \pi_5^*$	0.010	0.010	0.012	0.006	0.0040	0.0041	5.00
	$S_2$	$\pi_1^1 \pi_2^2 \pi_3^2 \pi_4^{*1}$ $\pi_1^2 \pi_2^1 \pi_3^1 \pi_4^{*2}$ $\pi_1^2 \pi_2^2 \pi_4^{*1} \pi_5^{*1}$ $\pi_1^2 \pi_2^2 \pi_3^1 \pi_6^{*1}$	$\pi_1 \rightarrow \pi_4^*$ $\pi_2 \pi_3 \rightarrow \pi_4^{*2}$ $\pi_3 \rightarrow \pi_4^* \pi_5^*$ $\pi_3 \rightarrow \pi_6^*$	0.016	0.014	0.023	0.011	0.0006	0.0008	8.17
	$S_3$	$\pi_1^1 \pi_2^2 \pi_3^2 \pi_5^{*1}$ $\pi_1^2 \pi_3^2 \pi_5^{*2}$ $\pi_1^2 \pi_2^1 \pi_3^2 \pi_6^{*1}$ $\pi_1^2 \pi_2^1 \pi_3^1 \pi_4^{*1} \pi_5^{*1}$	$\pi_1 \rightarrow \pi_5^*$ $\pi_2^2 \rightarrow \pi_5^{*2}$ $\pi_2 \rightarrow \pi_6^*$ $\pi_2 \pi_3 \rightarrow \pi_4^* \pi_5^*$	0.016	0.013	0.027	0.013	0.0006	0.0008	8.17
	$S_7$	$\pi_1^2 \pi_2^1 \pi_3^1 \pi_4^{*1} \pi_5^{*1}$	$\pi_2 \pi_3 \rightarrow \pi_4^* \pi_5^*$	0.045	0.032	0.025	0.009	0.0009	0.0029	11.51
Triplet	State	Configuration	Excitation	PDI <sup>A</sup>	PDI <sup>F</sup>	FLU <sup>A</sup>	FLU <sup>F</sup>	$I_{\text{ring}}$	MCI	$\Delta E(\text{eV})$
$C_6H_6$ $D_{6h}$	$T_1$	$\pi_1^2 \pi_2^1 \pi_3^2 \pi_5^{*1}$	$\pi_2 \rightarrow \pi_5^*$	0.018	0.015	0.033	0.020	0.0027	0.0023	3.55
	$T_2$	$\pi_1^2 \pi_2^2 \pi_3^1 \pi_5^{*1}$ $\pi_1^2 \pi_2^1 \pi_3^2 \pi_4^{*1}$	$\pi_3 \rightarrow \pi_5^*$ $\pi_2 \rightarrow \pi_4^*$	0.010	0.010	0.014	0.007	0.0042	0.0043	5.25
	$T_3$	$\pi_1^2 \pi_2^2 \pi_3^1 \pi_4^{*1}$	$\pi_3 \rightarrow \pi_5^*$	0.031	0.022	0.014	0.007	0.0029	0.0025	5.49
	$T_4$	$\pi_1^1 \pi_2^2 \pi_3^2 \pi_5^{*1}$ $\pi_1^2 \pi_2^1 \pi_3^2 \pi_6^{*1}$	$\pi_1 \rightarrow \pi_5^*$ $\pi_2 \rightarrow \pi_6^*$	0.028	0.019	0.026	0.014	0.0011	0.0014	6.94
Quintet	State	Configuration	Excitation	PDI <sup>A</sup>	PDI <sup>F</sup>	FLU <sup>A</sup>	FLU <sup>F</sup>	$I_{\text{ring}}$	MCI	$\Delta E(\text{eV})$
$C_6H_6$ $D_{6h}$	$Q_1$	$\pi_1^2 \pi_2^1 \pi_3^1 \pi_4^{*1} \pi_5^{*1}$	$\pi_2 \pi_3 \rightarrow \pi_4^* \pi_5^*$	0.041	0.027	0.034	0.016	0.0006	0.0020	7.88
	$Q_2$	$\pi_1^2 \pi_2^1 \pi_3^1 \pi_4^{*1} \pi_6^{*1}$ $\pi_1^1 \pi_2^2 \pi_3^1 \pi_4^{*1} \pi_5^{*1}$	$\pi_2 \pi_3 \rightarrow \pi_4^* \pi_6^*$ $\pi_1 \pi_3 \rightarrow \pi_4^* \pi_5^*$	0.012	0.011	0.035	0.015	0.0004	0.0005	10.63
	$Q_3$	$\pi_1^2 \pi_2^1 \pi_3^1 \pi_5^{*1} \pi_6^{*1}$ $\pi_1^1 \pi_2^1 \pi_3^2 \pi_4^{*1} \pi_5^{*1}$	$\pi_2 \pi_3 \rightarrow \pi_5^* \pi_6^*$ $\pi_1 \pi_2 \rightarrow \pi_4^* \pi_5^*$	0.012	0.011	0.035	0.015	0.0004	0.0005	10.63

Table 3. Values of PDI, FLU,  $I_{\text{ring}}$ , and MCI for low-lying singlet, triplet, quintet, and septet states of  $\text{C}_6\text{H}_6$ ,  $\text{C}_4\text{H}_4$ , and  $\text{C}_8\text{H}_8$  at the B3LYP/6-

311++g(d,p) level of theory. All units are in au.

B3LYP	State	PDI	FLU	$I_{\text{ring}}$	MCI	
$\text{C}_6\text{H}_6$	$S_0$	0.103	0.000	0.0478	0.0721	
	$D_{6h}$	$T_1$	0.038	0.025	0.0028	-0.0015
		$Q_1$	0.098	0.029	0.0011	0.0451
$\text{C}_4\text{H}_4$	$S_0$		0.104	0.0054	0.0101	
	$D_{2h}$	$T_1$		0.012	0.0385	0.1271
$\text{C}_8\text{H}_8$	$S_0$		0.051	0.0244	-0.0005	
	$D_{4h}$	$T_1$		0.001	0.0071	0.0271
		$Q_1$		0.029	0.0001	0.0013
		Septet <sub>1</sub>		0.033	0.0000	0.0178

Table 4. Values of PDI, FLU,  $I_{\text{ring}}$ , and MCI for low-lying singlet, triplet excited states of  $\text{C}_4\text{H}_4$ . Vertical excitation energies of singlet and triplet states have been calculated with respect to the singlet ground state energy. All units are in au, except  $\Delta E(\text{eV})$  and bond distances which are in eV and Å, respectively.

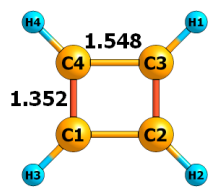
Singlet	State	Configuration	Excitation	FLU <sup>A</sup>	FLU <sup>F</sup>	$I_{\text{ring}}$	MCI	$\Delta E$ (eV)
$\text{C}_4\text{H}_4$	$S_0$	$\pi_1^2\pi_2^2$		0.062	0.036	0.0063	0.0092	0.00
	$S_1$	$\pi_1^2\pi_3^{*2}$	$\pi_2^2 \rightarrow \pi_3^{*2}$	0.024	0.011	0.0066	0.0101	4.28
	$S_2$	$\pi_1^2\pi_2^1\pi_3^{*1}$	$\pi_2 \rightarrow \pi_3^*$	0.009	0.003	0.0447	0.0491	4.61
	$S_3$	$\pi_1^2\pi_2^1\pi_4^{*1}$	$\pi_2 \rightarrow \pi_4^*$	0.038	0.021	0.0039	0.0096	5.83
		$\pi_1^1\pi_2^2\pi_3^{*1}$	$\pi_1 \rightarrow \pi_3^*$					
Triplet	State	Configuration	Excitation	FLU <sup>A</sup>	FLU <sup>F</sup>	$I_{\text{ring}}$	MCI	$\Delta E$ (eV)
$\text{C}_4\text{H}_4$	$T_1$	$\pi_1^2\pi_2^1\pi_3^{*1}$	$\pi_2 \rightarrow \pi_3^*$	0.014	0.009	0.0330	0.0361	0.75
$\text{D}_{2h}$	$T_2$	$\pi_1^2\pi_3^{*1}\pi_4^{*1}$	$\pi_2^2 \rightarrow \pi_3^*\pi_4^*$	0.039	0.021	0.0031	0.0037	4.57
		$\pi_1^1\pi_2^1\pi_3^{*2}$	$\pi_1\pi_2 \rightarrow \pi_3^{*2}$					
	$T_3$	$\pi_1^2\pi_2^{*1}\pi_4^{*1}$	$\pi_2 \rightarrow \pi_4^*$	0.039	0.021	0.0031	0.0037	4.57
		$\pi_1^1\pi_2^2\pi_3^{*1}$	$\pi_1 \rightarrow \pi_3^*$					
$T_4$	$\pi_1^1\pi_2^1\pi_3^{*2}$	$\pi_1\pi_2 \rightarrow \pi_3^{*2}$	0.041	0.020	0.0054	0.0054	9.67	
		$\pi_1^2\pi_2^{*1}\pi_4^{*1}$	$\pi_2 \rightarrow \pi_4^*$					

Table 5. Values of PDI, FLU,  $I_{\text{ring}}$ , and MCI for low-lying singlet, triplet, quintuplet, and septet excited states of  $\text{C}_8\text{H}_8$ . Vertical excitation energies have been calculated with respect to the singlet ground state energy. All units are in au, except  $\Delta E$ (eV) and bond distances which are in eV and Å, respectively.

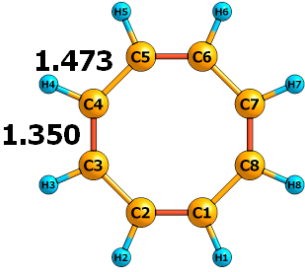
Singlet	State	Configuration	Excitation	FLU <sup>A</sup>	FLU <sup>F</sup>	$I_{\text{ring}}$	MCI	$\Delta E$
$\text{C}_8\text{H}_8$	$S_0$	$\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2$		0.041	0.024	0.0011	0.0005	
	$S_1$	$\pi_1^2 \pi_2^2 \pi_3^2 \pi_5^{*2}$	$\pi_4^2 \rightarrow \pi_5^{*2}$	0.010	0.007	0.0020	0.0001	2.97
	$S_2$	$\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^1 \pi_5^{*1}$	$\pi_4 \rightarrow \pi_5^*$	0.002	0.002	0.0054	0.0061	3.82
	$S_3$	$\pi_1^2 \pi_2^1 \pi_3^2 \pi_4^2 \pi_5^{*1}$ $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^1 \pi_5^{*2}$	$\pi_2 \rightarrow \pi_5^*$ $\pi_3 \pi_4 \rightarrow \pi_5^{*2}$	0.011	0.005	0.0005	0.0006	5.79
Triplet	State	Configuration	Excitation	FLU <sup>A</sup>	FLU <sup>F</sup>	$I_{\text{ring}}$	MCI	$\Delta E$
$\text{C}_8\text{H}_8$	$T_1$	$\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^1 \pi_5^{*1}$	$\pi_4 \rightarrow \pi_5^*$	0.004	0.003	0.0033	0.0047	1.60
$\text{D}_{4h}$	$T_2$	$\pi_1^2 \pi_2^2 \pi_3^1 \pi_4^2 \pi_5^{*1}$	$\pi_3 \rightarrow \pi_5^*$	0.039	0.014	0.0004	0.0004	4.00
		$\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^1 \pi_6^{*1}$	$\pi_4 \rightarrow \pi_6^*$					
$\text{D}_{4h}$	$T_3$	$\pi_1^2 \pi_2^1 \pi_3^2 \pi_4^2 \pi_5^{*1}$	$\pi_2 \rightarrow \pi_5^*$	0.039	0.014	0.0004	0.0004	4.00
		$\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^1 \pi_6^{*1}$	$\pi_4 \rightarrow \pi_6^*$					
	State	Configuration	Excitation	FLU <sup>A</sup>	FLU <sup>F</sup>	$I_{\text{ring}}$	MCI	$\Delta E$
$\text{C}_8\text{H}_8$	$Q_1$	$\pi_1^2 \pi_2^2 \pi_3^1 \pi_4^1 \pi_5^{*1} \pi_6^{*1}$ $\pi_1^2 \pi_2^1 \pi_3^2 \pi_4^1 \pi_5^{*1} \pi_7^{*1}$	$\pi_3 \pi_4 \rightarrow \pi_5^* \pi_6^*$ $\pi_2 \pi_4 \rightarrow \pi_5^* \pi_7^*$	0.021	0.013	0.0001	0.0002	8.26
$\text{D}_{4h}$	Septet <sub>1</sub>	$\pi_1^2 \pi_2^1 \pi_3^1 \pi_4^1 \pi_5^{*1} \pi_6^{*1} \pi_7^{*1}$	$\pi_2 \pi_3 \pi_4 \rightarrow \pi_5^* \pi_6^* \pi_7^*$	0.038	0.016	0.0000	0.0001	13.80

Figure 1. Molecular orbitals selected for the active space of (a)  $C_6H_6$ , (b)  $C_4H_4$ , and (c)  $C_8H_8$

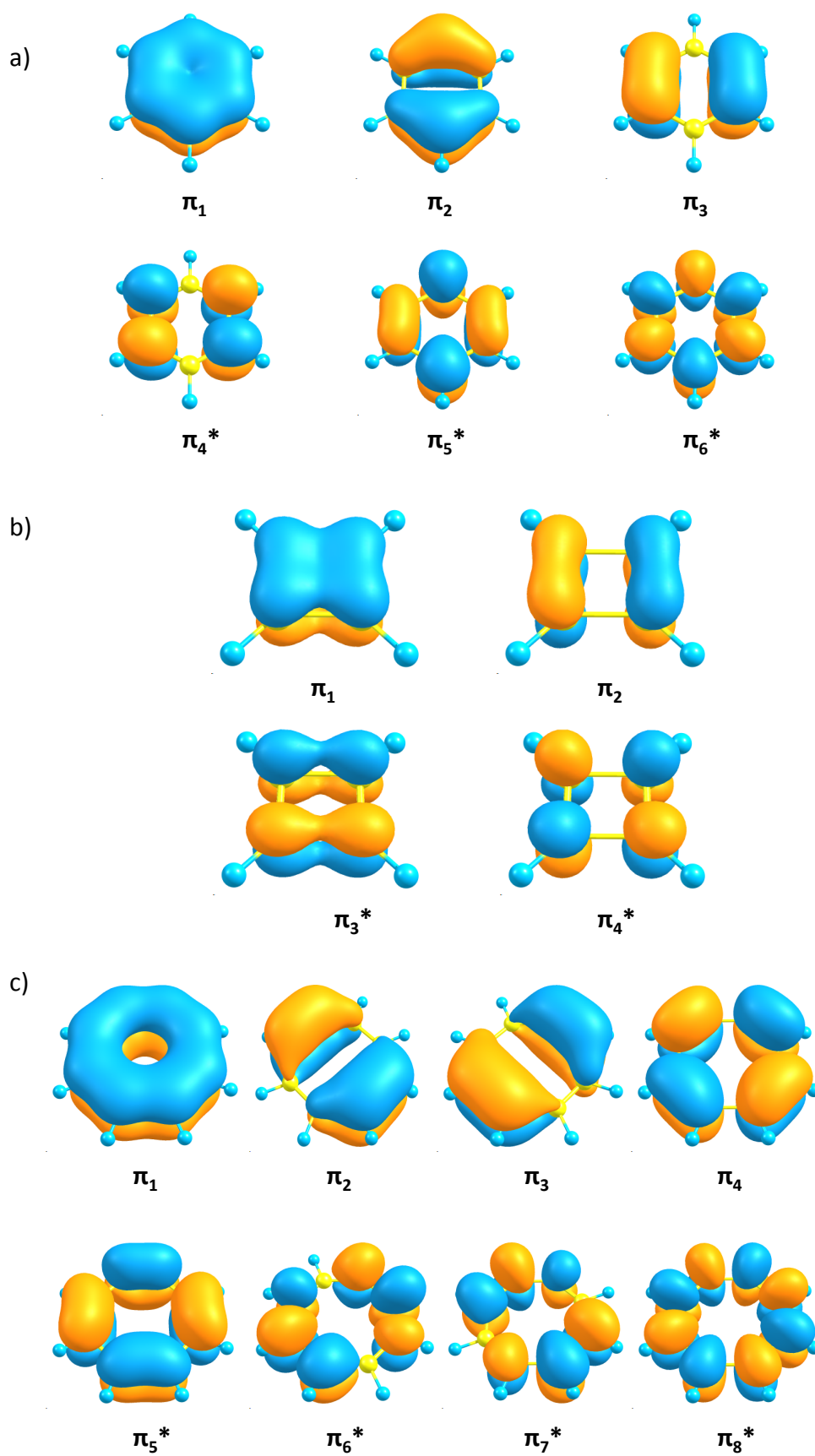




Figure 2. Values of  $\delta^F(\text{C,C})$  for the studied low-lying singlet, triplet, and quintet states of  $\text{C}_6\text{H}_6$ . Units are electrons.

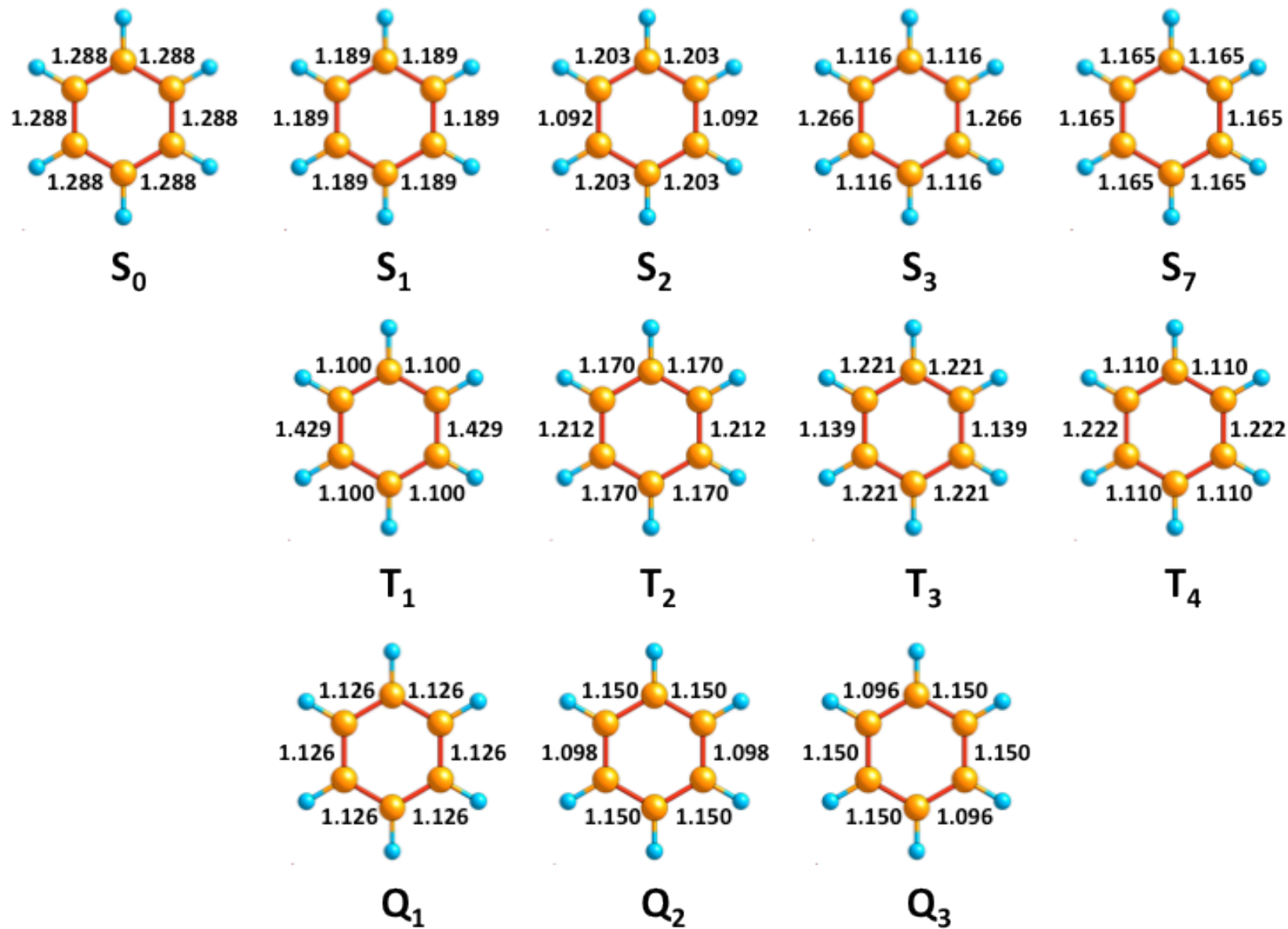


Figure 3. Values of  $\delta^F(\text{C,C})$  for the studied low-lying singlet and triplet states of  $\text{C}_4\text{H}_4$ . Units are electrons.

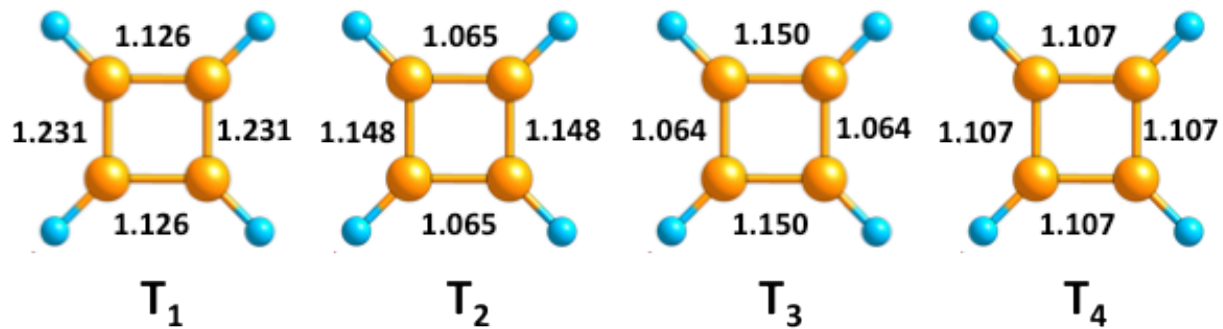
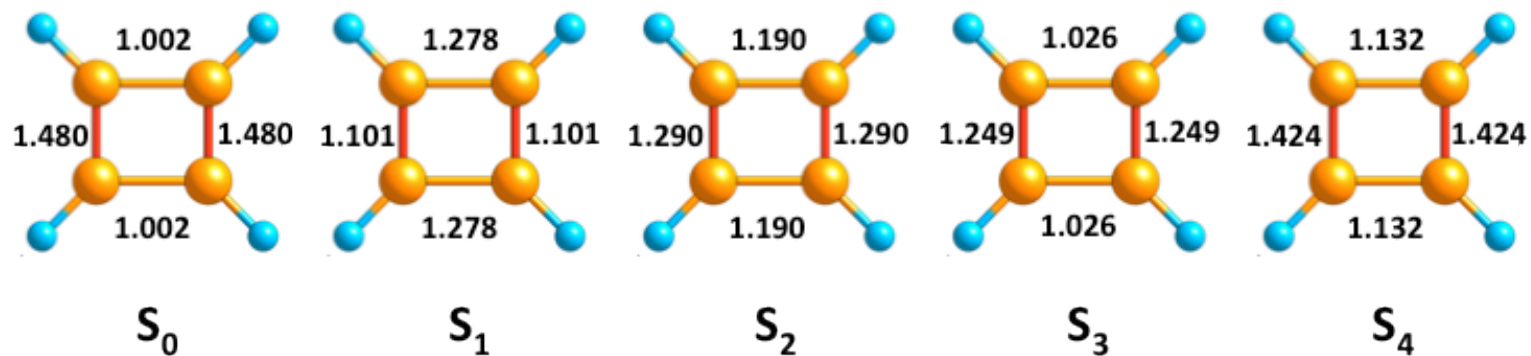


Figure 4. Values of  $\delta^F(\text{C,C})$  for the studied low-lying singlet, triplet, quintet, and septet states of  $\text{C}_8\text{H}_8$ . Units are electrons.

