


 Cite this: *RSC Adv.*, 2024, 14, 33741

# Aromatic stabilization energies in excited states at the multiconfigurational level: assessment in archetypal organic rings†

 Ricardo Pino-Rios  \*ab

In this study, the excited state (anti)aromaticity of archetypal rings: benzene, cyclobutadiene, and cyclooctatetraene, was investigated using the energetic criterion by calculating aromatic stabilization energies. Calculations were performed at the multiconfigurational level, including dynamic correlation effect corrections using the N-electron valence state perturbation theory (NEVPT2) method. Results were compared with previously published data based on the magnetic and delocalization criteria. Aromaticity was assessed for the ground state, singlet excited states ( $S_1$ ,  $S_2$ , and  $S_3$ ), and triplet excited states ( $T_1$ ,  $T_2$ ,  $T_3$ , and  $T_4$ ). (Anti)aromaticity assignments using the energetic criterion demonstrate both agreement and discrepancies with the other criteria, particularly for higher energy electronic states demonstrating the complexity of aromaticity assignment beyond the ground state. Finally, an approximate equation is proposed for the calculation of aromatic stabilization energies in excited states using experimental data such as formation enthalpies and well-resolved absorption spectra.

 Received 16th July 2024  
 Accepted 10th October 2024

DOI: 10.1039/d4ra05147e

[rsc.li/rsc-advances](https://rsc.li/rsc-advances)

## Introduction

The modulation of (anti)aromaticity in the ground and excited states has gained much attention in recent years as it opens the door to the intelligent design of new chemical compounds. The modification of ground-state aromaticity has an impact on excited-state antiaromaticity and *vice versa*. Moreover, the assembly between aromatic and antiaromatic units in the ground state has a clear effect on the electronic structure, which allows to obtain antiaromatic–aromatic species in excited states that can exhibit interesting photochemical properties.<sup>1–6</sup>

For the assignment of aromaticity, Hückel<sup>7</sup> and Baird<sup>8</sup> rules are the cornerstone. These rules *via* a simple electron ( $\pi$  for organic species) count determine whether a compound will be aromatic or antiaromatic. For more complex species such as polycyclic systems, we have other rules such as the Platt's perimeter<sup>9</sup> model, Clar's rules<sup>10,11</sup> for benzenoids and the Glidewell–Lloyd rule for systems containing non-benzenoid rings.<sup>12–14</sup>

More recently, several criteria have been developed to assign (anti)aromatic behavior and to quantify this property. These include magnetic,<sup>15</sup> delocalization,<sup>16,17</sup> energetic,<sup>18</sup> and other criteria.<sup>19–23</sup> The first two are the ones that have shown the

greatest development and popularity owing to their effectiveness in quantification and because of the simplicity of their computation due to the development of different programs.<sup>24–28</sup>

(Anti)aromaticity assignment in excited states is often complicated beyond the lowest energy excited states (beyond  $T_1$  or  $S_1$ ) mostly owing to the multiconfigurational character of electronic states, which requires the use of methods to account for these features, such as the complete active space self-consistent field (CASSCF) method.<sup>29</sup> Magnetic and delocalization criteria have had success since some indicators can be obtained using these multiconfigurational methods;<sup>30–32</sup> however, they have some disagreements concerning (anti)aromaticity assignments.<sup>30,33</sup>

The energetic criterion is probably the oldest quantitative criterion for the study of aromaticity, dating back to 1933 when Pauling and Wheland calculated the aromatic stabilization energy for benzene.<sup>34</sup> However, in many cases, the quantification of (anti)aromaticity using this criterion can be a non-trivial exercise, and in some cases, it only allows the study of the low-lying excited state.<sup>35,36</sup> This is primarily due to the need to use reference reactions that avoid the occurrence of effects unrelated to aromaticity and due to the complexity of calculations that need to be performed.<sup>18,23,35,37–40</sup>

Recently, the *fulvenization* approach<sup>41</sup> was proposed as a simple and reliable method for the calculation of isomerization stabilization energies (ISEs) originally proposed by Schleyer in 2002.<sup>37</sup> This approach uses as reference the fulvenic isomer of the N-membered ring to be studied. It is just as simple to obtain as the original but has certain advantages. For example, it allows the calculation of systems that the original method could

<sup>a</sup>Química y Farmacia, Facultad de Ciencias de la Salud, Universidad Arturo Prat, Casilla 121, Iquique, 1100000, Chile. E-mail: [rpinoorios@unap.cl](mailto:rpinoorios@unap.cl)

<sup>b</sup>Instituto de Ciencias Exactas y Naturales (ICEN), Universidad Arturo Prat, Playa Brava 3256, 1111346, Iquique, Chile

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ra05147e>



not calculate due to problems with the reference isomer. Additionally, the non-aromatic reference in the *fulvenization* (Fulv-ISE) approach is a planar conjugated system, which avoids the appearance of possible effects not related to (anti) aromaticity.

In this work, it is shown that this approach also allows assigning and quantifying the aromaticity in excited states through the use of multiconfigurational tools. For this purpose, the author quantified the (anti)aromaticity using the isomerization stabilization energies of the low-lying excited states of organic archetypes, namely, benzene, cyclobutadiene and cyclooctatetraene. The choice of multi-configurational methods over less computationally expensive techniques, such as time-dependent density functional theory (TD-DFT), stems from the limitations of the latter in accurately describing excited states. Different functionals can yield highly variable results, requiring comparison with experimental data. Moreover, the presence of ghost states in TD-DFT can lead to erroneous energy predictions. Although these ghost states can be mitigated using functionals with a high Hartree-Fock exchange component, there are instances where the predicted excitation energies still do not align closely with the experimental values.<sup>42–44</sup> Additionally, the main objective of this study is to quantify for the first time the (anti)aromaticity in electronic states beyond the first excited state as well as to compare the assignments delivered by this method with other (anti)aromaticity criteria in order to evaluate its performance. Therefore, it is advisable to use more robust tools when available.

## Computational methods

Geometrical optimizations have been carried out using Gaussian16 (ref. 45) at the PBE0 (ref. 46)/def2-TZVP<sup>47</sup> level. The cases of cyclobutadiene (C<sub>4</sub>H<sub>4</sub>) and cyclooctatetraene (C<sub>8</sub>H<sub>8</sub>) were optimized at two different symmetries. D<sub>4h</sub> and D<sub>2h</sub> symmetries were used for the former, while geometries in D<sub>8h</sub> and D<sub>4h</sub> symmetries were used for the latter. For the case of benzene, the D<sub>6h</sub> symmetry was preserved. The CASSCF calculations were then performed with the PBE0 geometries (Franck-Condon approximation) using the ORCA program.<sup>48</sup> The active space used corresponds to all the π-electrons and orbitals possessed by each of the systems: (6,6) for C<sub>6</sub>H<sub>6</sub>, (4,4) for C<sub>4</sub>H<sub>4</sub>, and (8,8) for C<sub>8</sub>H<sub>8</sub> and for their respective fulvene isomers (for this, the rotate command was used so that the π-orbitals correspond to active space, see Fig. S1–S16 in the ESI†). State-average approach was employed (all electronic states contribute equally) and the resolution of identity approximation in conjunction with the def2-TZVP basis, which includes auxiliary functions for a reduction in the computational cost. The calculated states correspond to the fundamental S<sub>0</sub> and the vertical S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>, T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>, and T<sub>4</sub> states, which have been made separately according to their multiplicities, and the weights were assigned equally.

Energy corrections due to the inclusion of dynamic correlation effects have been made following the N-electron valence state perturbation theory (NEVPT2).<sup>49</sup> The calculation of the aromatic stabilization energies under the *fulvenization*

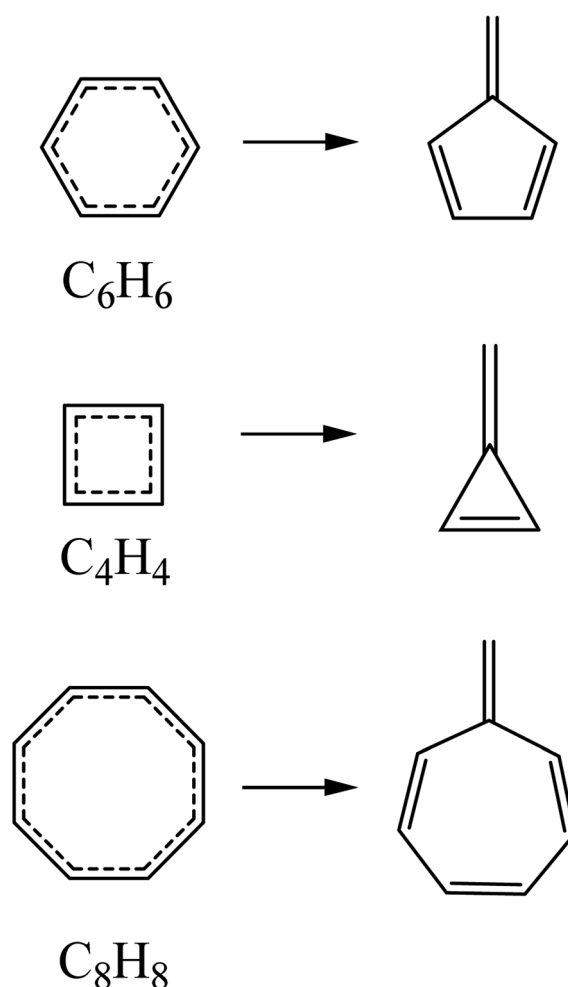
approach are obtained from the isomerization energy when an N-atom ring converts into its fulvenic isomer. The equation for obtaining the energies is shown below

$$\Delta E^{\text{Fulv-ISE}} = E^{\text{Fulv-Isomer}} - E^{\text{N-Ring}} \quad (1)$$

where  $E^{\text{Fulv-Isomer}}$  refers to the electronic energy of the fulvenic isomer in the required electronic state and  $E^{\text{N-Ring}}$  is the electronic energy of the ring to be studied in its respective electronic state. A positive value means that a system exhibits aromatic behavior, negative values and values close to zero, which indicates anti-aromaticity and non-aromaticity, respectively.

## Results and discussion

The results obtained through the application of the *fulvenization* approach have been compared with those obtained with the magnetic and delocalization criteria reported in the literature. The reference reactions used for the quantification of aromaticity using isomerization stabilization energies through the *fulvenization* approach of the ground state and the vertical excited states correspond to those presented in Scheme 1.



Scheme 1 Reference reactions used for the calculation of aromatic stabilization energies using the *fulvenization* approach.



Excited state energies including corrections for dynamic correlation effects (NEVPT2) offer better agreement with the available experimental/computational data<sup>31,32,50–52</sup> with respect to CASSCF (see Tables S1 and S3 in the ESI†). For this reason, the quantification of (anti)aromatic (de)stabilization was calculated at this level.

Initially, the values of Fulv-ISE for benzene and its respective electronic states configurations can be found in Table 1. For the case of  $S_0$ , the value is similar to that reported previously, indicating an aromatic behavior, while for the case of  $T_1$ , the value is different from that reported at the DFT level;<sup>41</sup> however, since it is a negative value, it is consistent with the antiaromatic character. For the case of  $S_1$ , the values reported by Karadakov *et al.*<sup>33</sup> and Feixas *et al.*<sup>30</sup> using the magnetic and delocalization criteria respectively indicate antiaromaticity; however, the value obtained under the *fulvenization* approach is  $-5.2$  kcal mol<sup>-1</sup>, suggesting a slightly antiaromatic or even non-aromatic behaviour. In the original article where the *fulvenization* approach was proposed, calculations of non-aromatic systems were not performed; however, in this work, it is shown that the aromatic stabilization energies obtained under this approach present values of  $-3.4$  and  $-0.4$  kcal mol<sup>-1</sup> for cyclohexene and cyclohexadiene, respectively (see Fig. S17 in ESI†), thus providing a small range ( $-4.7$  to  $0.0$  kcal mol<sup>-1</sup>) for the recognition of non-aromatic compounds at the DFT level.

Regarding  $S_2$ , the magnetic criteria indicates that in this state, benzene is aromatic, while the delocalization criterion indicates antiaromaticity. Using Fulv-ISE, a value of  $35.5$  kcal mol<sup>-1</sup> is obtained; thus, this electronic state would present an aromatic behavior in agreement with the magnetic criterion. It is necessary to mention that the delocalization criterion indicates that  $S_2$  and  $S_3$  are antiaromatic because the CASSCF

calculations reported by Feixas *et al.*<sup>30</sup> indicate that both states are degenerate; however, the calculations obtained in this work at the CASSCF level show a difference of  $0.2$  eV between  $S_2$  and  $S_3$ , which becomes even more noticeable when the dynamic correlation effects are included ( $1.7$  eV). In the case of  $S_3$ , a value of  $-22.4$  kcal mol<sup>-1</sup> is obtained; thus, it would be an antiaromatic state. This assignment is in agreement with Feixas *et al.* under the delocalization criteria while for the magnetic criterion, no values have been reported. The electronic delocalization indices also indicate that the  $T_2$ ,  $T_3$  and  $T_4$  states are antiaromatic.

Special attention must be paid to the case of  $T_2$  and  $T_3$ , which are degenerate states with excitation energies of  $5.1$  eV at the NEVPT2 level. The *fulvenization* approach indicates that despite this degeneracy, the assignments are antiaromatic/non-aromatic for the case of  $S_2$  and aromatic for the case of  $S_3$  (see Table 1). These differences can be attributed to the non-degenerate electronic states of the reference fulvene; thus, it is possible that under this criterion, one has different (anti) aromaticity assignments, which could result in a limitation of the method in highly symmetric systems. The same pattern will be observed later for the case of cyclooctatetraene. For the case of  $T_4$ , the value obtained is  $62.4$  kcal mol<sup>-1</sup>, which indicates an aromatic behavior; however, due to the results and the possible degeneracies between the electronic states, it is recommended that for the assignment of (anti)aromaticity of  $N$  electronic states, at least  $N + 1$  states should be calculated.

The Fulv-ISE values for the  $S_0$  and  $T_1$  states of  $C_4H_4$  reported in Table 2 are in agreement with the Hückel and Baird rules; on the other hand, the singlet excited states in all cases indicate aromaticity for both  $D_{4h}$  and  $D_{2h}$  symmetry. Some discrepancies are observed when compared with the magnetic and delocalization criteria. The states  $S_1$ ,  $S_2$  and  $S_3$  present aromatic behavior according to Fulv-ISE; however, Karadakov *et al.*<sup>33</sup> indicated aromaticity for  $S_1$  and antiaromaticity for  $S_2$  (they do

Table 1 Aromatic stabilization energies under the *fulvenization* approach (in kcal mol<sup>-1</sup>) and electronic state occupations for benzene at the NEVPT2/def2-TZVP//PBE0/def2-TZVP level

| $C_6H_6$ ( $D_{6h}$ ) |  |          |
|-----------------------|--|----------|
| State                 | Configuration                                | Fulv-ISE |
| $S_0$                 | $\pi_1^2\pi_2^2\pi_3^2\pi_4^0\pi_5^0\pi_6^0$ | 34.5     |
| $S_1$                 | $\pi_1^2\pi_2^1\pi_3^2\pi_4^1\pi_5^0\pi_6^0$ | -5.2     |
| $S_2$                 | $\pi_1^2\pi_2^2\pi_3^1\pi_4^0\pi_5^0\pi_6^0$ | 35.5     |
| $S_3$                 | $\pi_1^2\pi_2^2\pi_3^2\pi_4^0\pi_5^0\pi_6^0$ | -22.4    |
| $T_1$                 | $\pi_1^2\pi_2^2\pi_3^1\pi_4^1\pi_5^0\pi_6^0$ | -8.5     |
| $T_2$                 | $\pi_1^2\pi_2^2\pi_3^2\pi_4^1\pi_5^0\pi_6^0$ | -5.5     |
| $T_3$                 | $\pi_1^2\pi_2^2\pi_3^1\pi_4^1\pi_5^0\pi_6^0$ | 51.2     |
| $T_4$                 | $\pi_1^2\pi_2^2\pi_3^2\pi_4^1\pi_5^0\pi_6^0$ | 62.5     |

Table 2 Aromatic stabilization energies under the *fulvenization* approach (in kcal mol<sup>-1</sup>) and electronic state occupations for cyclobutadiene at the NEVPT2/def2-TZVP//PBE0/def2-TZVP level

| $C_4H_4$ |          |                                |          |          |                                |
|----------|----------|--------------------------------|----------|----------|--------------------------------|
| $D_{4h}$ |          |                                | $D_{2h}$ |          |                                |
| State    | Fulv-ISE | Configuration                  | State    | Fulv-ISE | Configuration                  |
| $S_0$    | -30.7    | $\pi_1^2\pi_2^1\pi_3^1\pi_4^0$ | $S_0$    | -14.1    | $\pi_1^2\pi_2^2\pi_3^0\pi_4^0$ |
| $S_1$    | 49.8     | $\pi_1^2\pi_2^2\pi_3^0\pi_4^0$ | $S_1$    | 29.1     | $\pi_1^2\pi_2^1\pi_3^1\pi_4^0$ |
| $S_2$    | 98.8     | $\pi_1^2\pi_2^0\pi_3^2\pi_4^0$ | $S_2$    | 47.7     | $\pi_1^2\pi_2^0\pi_3^2\pi_4^0$ |
| $S_3$    | 38.2     | $\pi_1^2\pi_2^1\pi_3^0\pi_4^0$ | $S_3$    | 54.3     | $\pi_1^2\pi_2^1\pi_3^0\pi_4^1$ |
| $T_1$    | 50.7     | $\pi_1^2\pi_2^2\pi_3^0\pi_4^0$ | $T_1$    | 31.7     | $\pi_1^2\pi_2^1\pi_3^1\pi_4^0$ |
| $T_2$    | -22.8    | $\pi_1^2\pi_2^1\pi_3^0\pi_4^1$ | $T_2$    | -17.3    | $\pi_1^2\pi_2^1\pi_3^0\pi_4^1$ |
| $T_3$    | 8.0      | $\pi_1^2\pi_2^2\pi_3^1\pi_4^0$ | $T_3$    | -17.3    | $\pi_1^2\pi_2^2\pi_3^1\pi_4^1$ |
| $T_4$    | 18.6     | $\pi_1^2\pi_2^0\pi_3^1\pi_4^1$ | $T_4$    | 16.1     | $\pi_1^2\pi_2^1\pi_3^1\pi_4^0$ |



not report values for  $S_3$ ). On the other hand, the study by Feixas *et al.*<sup>30</sup> indicates that there is antiaromaticity for  $S_1$  and  $S_3$  and aromaticity for  $S_2$ .

For the case of triplet excited states, the Fulv-ISE values and delocalization indices coincide in an antiaromatic assignment for  $T_2$ . For the case of  $T_3$  and  $T_4$ , the delocalization criterion indicates antiaromaticity, while the energy criterion applied in this work indicates aromaticity. However, when switching from  $D_{4h}$  to  $D_{2h}$  symmetry, curiously, the  $T_3$  state becomes antiaromatic, coinciding with the delocalization criterion whose values were obtained at this symmetry. This switch from aromaticity to antiaromaticity in  $T_3$  is due to different electronic transitions. However, due to the inclusion of dynamic correlation effects, the occupancies of the states obtained in this work with respect to the one performed by Feixas *et al.* are different, which may explain the differences with respect to the aromaticity assignment.

The case of  $C_8H_8$  is less controversial since the  $D_{8h}$  symmetry coincides perfectly with the magnetic criterion. The  $S_0$  state is antiaromatic while the  $T_1$ ,  $S_1$  and  $S_2$  states are aromatic; indeed, Karadakov *et al.*<sup>53</sup> report that  $S_2$  is much more aromatic than  $T_1$  and  $S_1$  and the Fulv-ISE value for  $S_2$  is much higher when compared to the other two electronic states with  $D_{8h}$  symmetry. The delocalization criterion indicates that  $S_1$  as well as  $T_2$  and  $T_3$  are antiaromatic (no values are reported for  $T_4$  in Karadakov *et al.*'s work). The results with Fulv-ISE agree with the assignment given for  $T_2$  and  $T_3$ ; however, for the case of  $T_3$ , the value for  $D_{8h}$  symmetry is close to zero; therefore, in this symmetry, it could be considered non-aromatic, but if we reduce the

Table 4 Experimental enthalpies of formation ( $\Delta H_f$ ) and excited state energies (in kcal mol<sup>-1</sup>) for benzene and fulvene

| Compound | $\Delta H_f$ | $S_1$ | $S_2$ | $T_1$ | $T_2$ |
|----------|--------------|-------|-------|-------|-------|
| Benzene  | 19.8         | 119.9 | 143.0 | 92.2  | 110.7 |
| Fulvene  | 53.5         | 79.3  | 121.8 | 54.2  | 71.5  |
| Eqn (4)  | 33.7         | -6.9  | 12.5  | -4.3  | -5.5  |

symmetry to  $D_{4h}$ , the value becomes more negative. The opposite case is presented in  $T_1$  wherein on reducing the symmetry to  $D_{4h}$ , the value obtained indicates a non-aromatic behavior.  $T_4$  is an electronic state that presents antiaromaticity, becoming even more antiaromatic when going from  $D_{8h}$  to  $D_{4h}$  symmetry (Table 3).

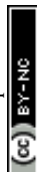
A relationship between the aromatic stabilization energies derived from the *fulvenization* approach and experimental data is proposed. Initially, it was suggested that the aromatic stabilization energy in the ground state could be estimated using experimental enthalpies of formation. For benzene in its ground state, this approach yields a value of 33.7 kcal mol<sup>-1</sup>, which is in excellent agreement with the energy calculated at the PBE0/def2-TZVP level (33.2 kcal mol<sup>-1</sup>). Consequently, eqn (1) can be approximated as follows.

$$\Delta E^{\text{Fulv-ISE}} \approx \Delta H_f^{\text{Fulv-isomer}} - \Delta H_f^{\text{N-ring}} \quad (2)$$

Additionally, the energies of the excited electronic states can be obtained from

Table 3 Aromatic stabilization energies under the *fulvenization* approach (in kcal mol<sup>-1</sup>) and electronic state occupations for cyclooctatetraene at the NEVPT2/def2-TZVP//PBE0/def2-TZVP level

| $C_8H_8$ |          |   |          |          |   |
|----------|----------|---|----------|----------|---|
| $D_{8h}$ |          |   | $D_{4h}$ |          |   |
| State    | Fulv-ISE | Configuration   | State    | Fulv-ISE | Configuration   |
| $S_0$    | -31.5    | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ | $S_0$    | -23.3    | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ |
| $S_1$    | 24.5     | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ | $S_1$    | 11.4     | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ |
| $S_2$    | 66.5     | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ | $S_2$    | 30.7     | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ |
| $S_3$    | -3.8     | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ | $S_3$    | -15.8    | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ |
| $T_1$    | 13.6     | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ | $T_1$    | -0.3     | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ |
| $T_2$    | -43.6    | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ | $T_2$    | -45.8    | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ |
| $T_3$    | -0.9     | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ | $T_3$    | -3.1     | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ |
| $T_4$    | -2.6     | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ | $T_4$    | -28.4    | $\pi_1^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2 \pi_7^2 \pi_8^2$ |



$$E_{\text{state}} = E_0 + \Delta E_{\text{exc}} \quad (3)$$

where  $E_0$  is the ground state energy and  $\Delta E_{\text{exc}}$  refers to the excitation energy. The aromatic stabilization energy in the excited states under the *fulvenization* approach can be approximated as follows.

$$\Delta E_{\text{exc}}^{\text{Fulv-ISE}} \approx (\Delta H_{\text{f}}^{\text{Fulv-isomer}} - \Delta H_{\text{f}}^{\text{N-ring}}) + (\Delta E_{\text{exc}}^{\text{Fulv-isomer}} - \Delta E_{\text{exc}}^{\text{N-isomer}}) \quad (4)$$

where the excitation energies could be taken from the well-resolved absorption spectra of the ring to be studied and its respective fulvenic isomer. As an example, we will calculate the  $\Delta E^{\text{Fulv-ISE}}$  values for benzene. The enthalpies of formation were obtained from the NIST database, while the excitation energies for both benzene and fulvene were sourced from a literature review of well-resolved spectra.<sup>50,51,54–56</sup> These experimental energies, along with the results obtained using eqn (4), are summarized in Table 4. As shown, the experimental data follow the same trends as the calculations, although there are differences in the absolute values. These discrepancies can be attributed to several factors, including experimental conditions and instrument resolution. This demonstrates that estimating (anti)aromaticity in excited states using experimental data is feasible, but it should be approached with caution. Ideally, such experiments should be performed under same conditions to minimize potential variations.

## Conclusions

The capacity of the recently proposed *fulvenization* approach for calculating the aromatic stabilization energies (Fulv-ISE) and assigning (anti)aromaticity in vertical excited states has been tested using three archetypal rings, namely, benzene, cyclobutadiene and cyclooctatetraene. The calculated energies were obtained through multiconfigurational calculations including dynamic correlation effect corrections (NEVPT2). In all cases, there are agreements and differences with the magnetic and delocalization states, the latter especially in the case of higher energy electronic states due to the inclusion of dynamic correction effects and the occupancies of the electronic states being different. Additionally, this work once again shows the complexity of aromaticity assignment when going beyond the ground state.

Results indicate that benzene shows aromaticity in the  $S_0$ ,  $S_2$ ,  $T_3$  and  $T_4$  vertical states, while the other computed states show antiaromatic behavior. Regarding the degenerate states  $T_2$  and  $T_3$ , different assignments are given since fulvene does not show degeneracy in these states, resulting in a limitation of the method due to the use of reference isomers. Additionally, it is recommended that if the  $N$  electronic states are to be analyzed, at least  $N + 1$  states should be calculated to confirm that the states do not exhibit degeneracy.

In the case of cyclobutadiene, all the calculated states present aromaticity with the exception of  $S_0$  and  $T_2$ ; however, the  $T_3$  state, which presents aromaticity in  $D_{4h}$  symmetry, becomes antiaromatic in  $D_{2h}$  symmetry. Cyclooctatetraene, on

the other hand, presents an aromatic character only in the  $S_1$  and  $S_2$  states, in agreement with the magnetic criterion, while the rest of the results at  $D_{8h}$  symmetry present antiaromaticity. In addition, it is shown that the aromatic stabilization energies under this approach can be obtained from the experimental data such as formation enthalpies and absorption peaks in well-resolved absorption spectra.

These results extend the capability of the energy criterion for aromaticity assignment beyond the first excited states. In addition, the aromatic stabilization energies for higher energy electronic states can be calculated in a straightforward manner.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The author thanks the financial support of the National Agency for Research and Development (ANID) through FONDECYT Project 1230571.

## References

- H. Ottosson, *Nat. Chem.*, 2012, **4**(12), 969–971.
- M. Rosenberg, C. Dahlstrand, K. Kilså and H. Ottosson, *Chem. Rev.*, 2014, **114**(10), 5379–5425.
- W. Zeng, D. W. Szczepanik and H. Bronstein, *J. Phys. Org. Chem.*, 2023, **36**(1), e4441.
- J. Kim, J. Oh, A. Osuka and D. Kim, *Chem. Soc. Rev.*, 2022, **51**(1), 268–292.
- J. Yan, T. Slanina, J. Bergman and H. Ottosson, *Chem.–Eur. J.*, 2023, **29**(19), e202203748.
- D. Dunlop, L. Ludvíková, A. Banerjee, H. Ottosson and T. Slanina, *J. Am. Chem. Soc.*, 2023, **145**(39), 21569–21575.
- E. Hückel, *Z. Phys.*, 1931, **70**(3), 204–286.
- N. C. Baird, *J. Am. Chem. Soc.*, 1972, **94**(14), 4941–4948.
- J. R. Platt, *J. Chem. Phys.*, 1949, **17**(5), 484–495.
- E. Clar, *The Aromatic Sextet*, J. Wiley, 1972.
- M. Solà, *Front. Chem.*, 2013, **1**, 1–8.
- C. Glidewell and D. Lloyd, *Tetrahedron*, 1984, **40**(21), 4455–4472.
- R. Pino-Rios and M. Solà, *J. Phys. Chem. A*, 2021, **125**(1), 230–234.
- R. Báez-Grez and R. Pino-Rios, *Phys. Chem. Chem. Phys.*, 2024, 12162–12167.
- R. Gershoni-Poranne and A. Stanger, *Chem. Soc. Rev.*, 2015, **44**(18), 6597–6615.
- F. Feixas, E. Matito, J. Poater and M. Solà, *Chem. Soc. Rev.*, 2015, **44**(18), 6434–6451.



- 17 I. Casademont-Reig, E. Ramos-Cordoba, M. Torrent-Sucarrat and E. Matito, in *Aromaticity*, ed. I. Fernandez, Elsevier, 2021, pp. 235–259.
- 18 M. Alonso and I. Fernández, in *Aromaticity*, ed. I. Fernandez, Elsevier, 2021, pp. 195–235.
- 19 H. Szatyłowicz, P. A. Wierzchowicz and T. M. Krygowski, in *Aromaticity*, ed. I. Fernandez, Elsevier, 2021, pp. 71–99.
- 20 D. R. Roy and P. K. Chattaraj, in *Aromaticity*, ed. I. Fernandez, Elsevier, 2021, pp. 285–319.
- 21 D. Yu, T. Stuyver, C. Rong, M. Alonso, T. Lu, F. De Proft, P. Geerlings and S. Liu, *Phys. Chem. Chem. Phys.*, 2019, **21**(33), 18195–18210.
- 22 R. Báez-Grez and R. Pino-Rios, *ACS Omega*, 2022, **7**(25), 21939–21945.
- 23 H. Szatyłowicz, P. A. Wierzchowicz and T. M. Krygowski, *Sci*, 2022, 1–22.
- 24 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**(5), 580–592.
- 25 T. A. Keith, *AIMAll (Version 190213)*, Overland Park KS, USA, 2019, <https://aim.tkgristmill.com>.
- 26 D. Inostroza, V. García, O. Yañez, J. J. Torres-Vega, A. Vásquez-Espinal, R. Pino-Rios, R. Báez-Grez and W. Tiznado, *New J. Chem.*, 2021, **45**(18), 8345–8351.
- 27 M. Orozco-Ic, J. L. Cabellos and G. Merino, *Aromagnetic*, Cinvestav-Mérida, Mérida, Mexico, 2016.
- 28 E. Matito, *ESI-3D: Electron Sharing Indices Program for 3D Molecular Space Partitioning*, Institute of Computational Chemistry and Catalysis (IQCC), University of Girona, 2006.
- 29 J. W. Park, R. Al-Saadon, M. K. MacLeod, T. Shiozaki and B. Vlasisavljevich, *Chem. Rev.*, 2020, **120**(13), 5878–5909.
- 30 F. Feixas, J. Vandenbussche, P. Bultinck, E. Matito and M. Solà, *Phys. Chem. Chem. Phys.*, 2011, **13**(46), 20690–20703.
- 31 P. B. Karadakov, *J. Phys. Chem. A*, 2008, **112**(31), 7303–7309.
- 32 P. B. Karadakov, *J. Phys. Chem. A*, 2008, **112**(49), 12707–12713.
- 33 P. B. Karadakov, P. Hearnshaw and K. E. Horner, *J. Org. Chem.*, 2016, **81**(22), 11346–11352.
- 34 L. Pauling and G. W. Wheland, *J. Chem. Phys.*, 1933, **1**(6), 362–374.
- 35 Y. Mo and P. v. R. Schleyer, *Chem.–Eur. J.*, 2006, **12**(7), 2009–2020.
- 36 I. Fernández and G. Frenking, *Faraday Discuss.*, 2007, **135**(0), 403–421.
- 37 P. v. R. Schleyer and F. Pühlhofer, *Org. Lett.*, 2002, **4**(17), 2873–2876.
- 38 T. M. Krygowski and M. K. Cyrański, *Chem. Rev.*, 2001, **101**(5), 1385–1420.
- 39 Y. García-Rodeja and M. Solà, in *Exploring Chemical Concepts through Theory and Computation*, 2024, pp. 223–250.
- 40 A. R. Katritzky, K. Jug and D. C. Oniciu, *Chem. Rev.*, 2001, **101**(5), 1421–1450.
- 41 L. Leyva-Parra and R. Pino-Rios, *ACS Omega*, 2024, **9**(1), 1436–1442.
- 42 F. Furche and D. Rappoport, in *Theoretical and Computational Chemistry*, ed. M. Olivucci, Elsevier, 2005, pp. 93–128.
- 43 C. Adamo and D. Jacquemin, *Chem. Soc. Rev.*, 2013, **42**(3), 845–856.
- 44 M. Campetella, F. Maschietto, M. J. Frisch, G. Scalmani, I. Ciofini and C. Adamo, *J. Comput. Chem.*, 2017, **38**(25), 2151–2156.
- 45 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16, Revision C.02*, Gaussian, Inc., Wallingford, CT, 2016.
- 46 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**(13), 6158–6170.
- 47 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**(18), 3297–3305.
- 48 F. Neese, F. Wennmohs, U. Becker and C. Riplinger, *J. Chem. Phys.*, 2020, **152**(22), 224108.
- 49 C. Angeli, R. Cimraglia and J.-P. Malrieu, *Chem. Phys. Lett.*, 2001, **350**(3), 297–305.
- 50 E. N. Lassettre, A. Skerbele, M. A. Dillon and K. J. Ross, *J. Chem. Phys.*, 1968, **48**(11), 5066–5096.
- 51 J. P. Doering, *J. Chem. Phys.*, 1969, **51**(7), 2866–2870.
- 52 M. H. Palmer, S. V. Hoffmann, N. C. Jones, M. Coreno, M. de Simone and C. Grazioli, *J. Chem. Phys.*, 2019, **151**(8), 084304.
- 53 P. B. Karadakov and N. Preston, *Phys. Chem. Chem. Phys.*, 2021, **23**(43), 24750–24756.
- 54 R. D. Brown, P. J. Domaille and J. E. Kent, *Aust. J. Chem.*, 1970, **23**(9), 1707–1720.
- 55 F. Negri and M. Z. Zgierski, *J. Chem. Phys.*, 1995, **102**(13), 5165–5173.
- 56 K. R. Asmis, M. Allan, O. Schafer and M. Fülcher, *J. Phys. Chem. A*, 1997, **101**(11), 2089–2095.

