

Update for Isomerization Stabilization Energies: The *Fulvenization* Approach

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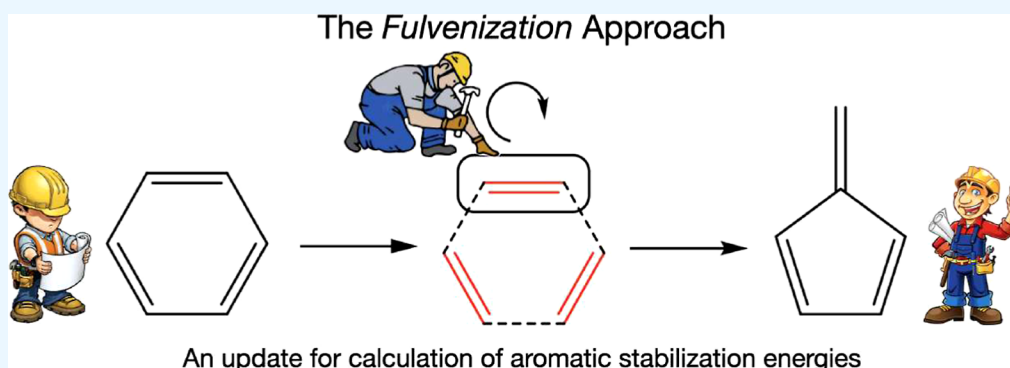
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ABSTRACT: An alternative approach for calculating aromatic stabilization energies is proposed based on transforming an (anti)aromatic ring into a fulvene isomer. This *fulvenization* process gives a value of $34.05 \text{ kcal}\cdot\text{mol}^{-1}$ for benzene in the singlet state and a value of $-17.85 \text{ kcal}\cdot\text{mol}^{-1}$ in the triplet state. Additionally, it is possible to use experimental values (as long as they exist) for the calculation as the gas-phase formation enthalpies of benzene and fulvene, whose difference is $33.72 \text{ kcal}\cdot\text{mol}^{-1}$. On the other hand, this same approach has been evaluated on several six-membered rings, including those persubstituted, biradicals, azines, and inorganic analogues, giving results in agreement with those reported in the literature using different criteria. Additionally, it is possible to differentiate the aromaticity of the rings in polycyclic aromatic hydrocarbons according to Clar's rules. Assigning the (anti)aromatic character in various nonbenzenoid rings (neutral and charged), except for five- and seven-membered rings, is also possible. The construction of the fulvene isomers in PAHs is set such that nonaromaticity-related effects are not considered. The results show that the *fulvenization* approach is an effective and efficient approach that can serve as an alternative or complement to existing tools.

INTRODUCTION

The energetic criterion for describing aromaticity in chemical compounds is one of the oldest criteria used to describe the stabilization of benzene due to its aromatic nature. The first aromatic stabilization energy (ASE) calculation for benzene was performed by Pauling and Wheland more than a century ago while developing the chemical theory of resonance.¹ After this cornerstone, different approaches (from both theoretical and experimental points of view) have been proposed. One of the most representative values is obtained through the experimental data with an ASE value of $36 \text{ kcal}\cdot\text{mol}^{-1}$.²

The calculation of ASEs is usually performed from reference reactions, being this one of its main limitations since, depending on the reference, different values can be obtained.³ On the other hand, effects not related to aromaticity could appear giving an over or underestimation of the stabilization energy, so this should be carried out with extreme caution.^{3,4} In some cases, the approach used for ASE in benzene cannot be extended to other aromatic systems. Finally, in more

modern approaches, computations are rather complicate, making the calculations a cumbersome exercise in many cases.⁵

In 2002, Schleyer and Pühlhofer proposed a simple and elegant way to calculate ASEs, the so-called isomerization stabilization energy (ISE),^{6,7} which, as its name indicates, is obtained from the difference between a methylated derivative of the aromatic ring and a nonaromatic isomer with an exocyclic double bond (see Figure 1).

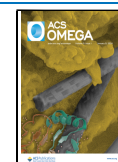
This approach allows the fast and efficient calculation of several compounds in singlet and triplet states. It has also been successfully applied to heterocyclic compounds,⁸ charged species,⁹ radical systems,¹⁰ metalloaromatic complexes,¹¹ and

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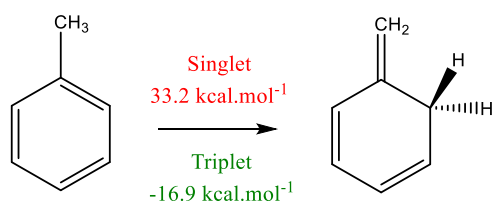


Figure 1. Isomerization stabilization energy (ISE) computed for benzene at the singlet (red) and triplet (green) states. Reproduced from ref 7. Copyright 2013 American Chemical Society.

polycyclic compounds.¹² However, this scheme also suffers from limitations. First, one of the carbons changes its hybridization from sp^2 to sp^3 , which could lead to the nonaromatic ring losing its planarity, and nonaromaticity effects could appear. Additionally, this scheme cannot be efficiently applied to substituted benzene systems such as formula C_6X_6 .^{6,7}

On the other hand, benzene is the lowest energy structure in its potential energy surface, which different authors have studied.¹³ The closest isomer is fulvene, a π -conjugated system with all its carbons presenting the same hybridization and a nonaromatic behavior. For this reason, the energetic difference between these two isomers can be considered to be an ASE. The calculation at the PBE0¹⁴/def2-TZVP¹⁵ level presents a value of $34.05 \text{ kcal}\cdot\text{mol}^{-1}$, similar to the value obtained experimentally and the value obtained using the scheme proposed by Schleyer.⁶ Likewise, this approach allows us to describe the antiaromatic character of benzene in the triplet state with a value of $-17.85 \text{ kcal}\cdot\text{mol}^{-1}$. We have carried out calculations using the functionals B3LYP,¹⁶ M06-2X,¹⁷ and ω B97X-D¹⁸ for benzene in singlet state whose values, respectively, are 33.77 , 34.22 , and $34.17 \text{ kcal}\cdot\text{mol}^{-1}$, showing that our scheme has no dependence on the functional.

It is also possible to use experimental data to obtain the ISE value. The NIST database indicates an enthalpy of formation value for benzene of $19.81 \text{ kcal}\cdot\text{mol}^{-1}$, while for fulvene, it is $53.53 \text{ kcal}\cdot\text{mol}^{-1}$, which gives an aromaticity stabilization value of $33.72 \text{ kcal}\cdot\text{mol}^{-1}$, which agrees with the calculated value and previous values reported in the literature.¹⁹

This scheme, where the aromatic ring is converted into a fulvene (*fulvenization* process), can be extended to various systems, including polycyclic aromatic hydrocarbons, heteroaromatics, and substituted benzenes. Figure 2 shows a practical way to obtain the respective fulvene from a given aromatic ring (benzene). One has the required conjugated system and selects one of the double bonds; this bond is “rotated” by 90° to obtain the desired fulvene. Another practical way of looking at it is that from an N -membered ring, the fulvene isomer is an $N-1$ -membered ring with an exocyclic double bond.

RESULTS AND DISCUSSION

The fulvenization process serves as a methodology for quantifying the aromaticity of the benzene derivatives. An example is found in the persubstituted benzenes when hydrogen atoms are replaced by fluorine atoms, which presents a reduction in its aromatic character ($25.09 \text{ kcal}\cdot\text{mol}^{-1}$), in agreement with previous studies applying the magnetic criteria and information-theoretic-based indicators.²⁰ A reduction in aromaticity is also observed when hydrogens are replaced by chlorine, cyano, and hydroxyls, whose values are 30.56 , 26.20 , and $26.18 \text{ kcal}\cdot\text{mol}^{-1}$, respectively (Figure S1 in the Supporting Information).²¹ Since a systematic study of the effect of substituents on the aromaticity of a ring using this scheme leads to a degree of arbitrariness; for example, in the study of 1,2 substituted benzenes, we recommend starting substitutions at the carbons most distant from the exocyclic bond. In addition, it is possible to quantify the aromaticity of biradical compounds such as benzyne, which have been studied recently using various criteria. The case of *o*-benzyne is striking because different construction schemes can give different results, and for this reason, it is recommendable to study aromaticity using different criteria as has been established by other authors.^{22,23} The best value for *o*-benzyne obtained is $30.75 \text{ kcal}\cdot\text{mol}^{-1}$, which is in agreement with the delocalization criterion at the CASSCF²⁴ (10,10)/def2-TZVP¹⁵ level. The reactions can be observed in Figure S2.^{10,25}

Additionally, it is possible to study azines; recently, it has been shown through a detailed analysis using the magnetic criterion that replacing a CH unit by an N atom in benzene results in a reduction in the aromaticity.²⁶ However, when applying the *fulvenization* approach (see Figure 3) to pyridine and diazines, it is possible to notice a considerable reduction in the aromatic character, being more notorious in the case of diazines, which, although they do not coincide in the order of aromaticity given by the magnetic criterion, it is possible to show the reduction in the aromaticity of these compounds. On the other hand, obtaining values of aromatic stabilization energies in inorganic benzene analogues is also possible, as is the case of Si_6H_6 and Ge_6H_6 in their D_{6h} symmetry (Figure S3). Although these structures are not local minimum on their potential energy surfaces, they are aromatic.²⁷ The values obtained for both systems at the PBE0/def2-TZVP level are $16.46 \text{ kcal}\cdot\text{mol}^{-1}$ and $17.34 \text{ kcal}\cdot\text{mol}^{-1}$, indicating low aromaticity when compared to benzene.²⁸

This *fulvenization* approach can be extended to polycyclic aromatic hydrocarbons to study the local rings. Take the case of naphthalene; the fulvenic isomer is constructed through the “twist” of a double bond, seeking that the conjugation of the adjacent ring is affected as little as possible in order to avoid an overestimation in the numerical value delivered. Using the scheme presented in Figure 4, the ISE value obtained for naphthalene is $23.03 \text{ kcal}\cdot\text{mol}^{-1}$ lower than that obtained for

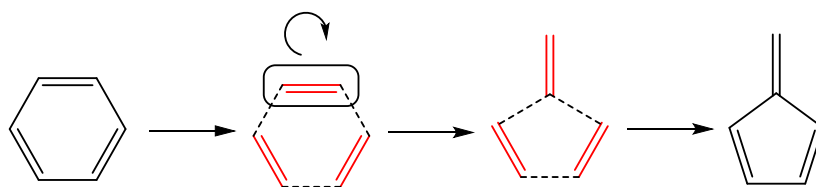


Figure 2. Fulvenization process of the ISE of benzene.

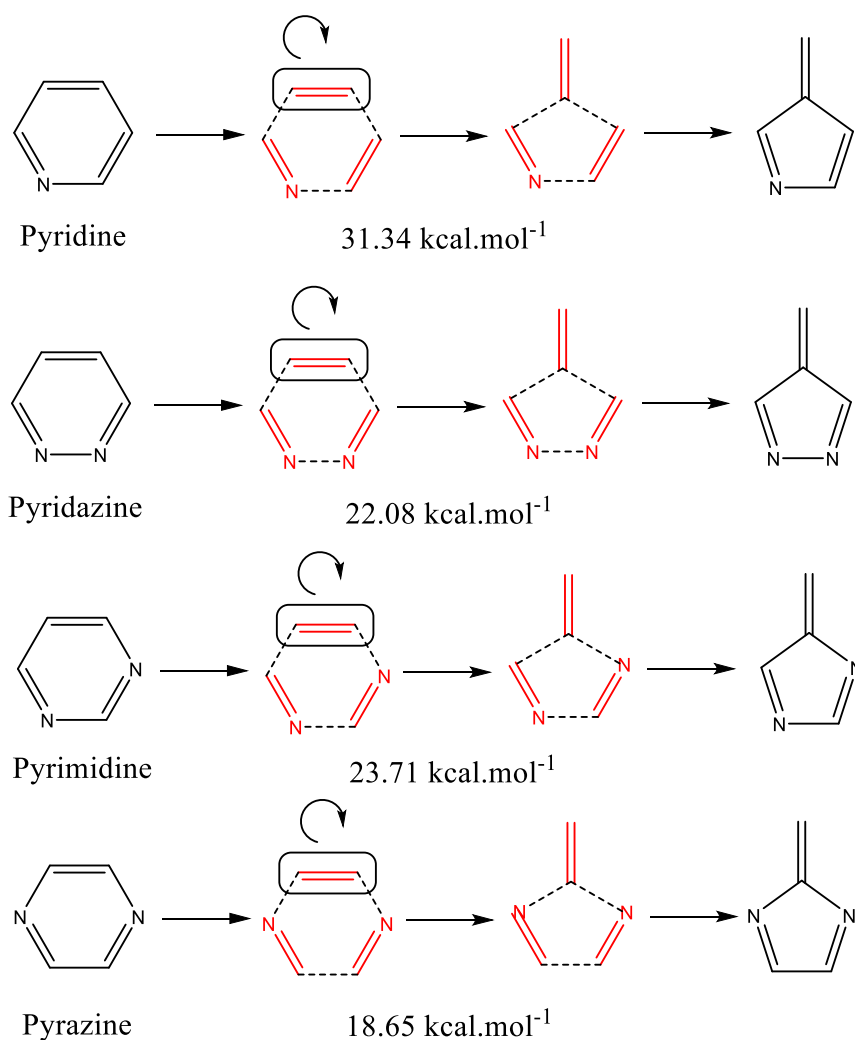


Figure 3. Fulvenization process of the ISE of pyridine and diazines.

benzene, consistent with the reduction of local aromaticity reported in the literature.^{29,30}

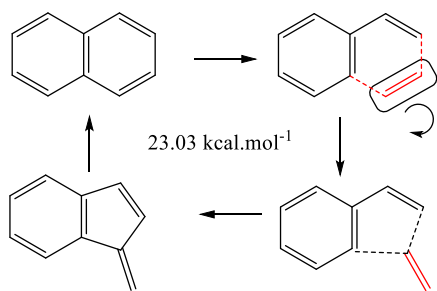


Figure 4. Fulvenization process of ISE for a local ring in naphthalene.

Additionally, it is possible to differentiate the stability of the aromatic rings into different isomers. Poater and Solá showed through delocalization criteria and energy decomposition analysis some years ago that kinked PAHs (phenanthrene family) are more stable than linear PAHs (anthracene family).³¹ It is known that, by Clar's rules, the outer rings are the major contributors to the aromaticity of the system.³² In the case of phenanthrene, using the ISEs (see Figure 5), it has a value of $37.39 \text{ kcal.mol}^{-1}$ very similar to benzene, i.e., the

benzenoid nature of this ring is maintained (only $4.1 \text{ kcal.mol}^{-1}$ above the benzene value). This result differs from those obtained through the reaction strategy proposed by Schleyer, which has shown a more significant overestimation of the aromatic stabilization value (about 8 kcal.mol^{-1} higher than benzene).^{6,23} It is necessary to mention that at the moment of building the respective fulvene isomer to obtain the ISE for the central ring, after optimization, the same compound was obtained (see Figure 5). The results obtained indicate a notorious reduction in the aromatic character according to the Clar rules.

Through the aromatic stabilization energies using the fulvenization strategy, it is possible to adequately describe Clar structures. For the case of pyrene and chrysene, the values of the outer rings are 35.48 and $38.86 \text{ kcal.mol}^{-1}$, respectively, while the central rings for both structures are 18.03 and $25.48 \text{ kcal.mol}^{-1}$, respectively. These results are in agreement with Clar's rules, which indicate that the most important resonant structures are those where the outer rings exhibit aromaticity.^{30,32,33} On the other hand, the aromaticity of the outer rings in coronene has a stabilization value of $35.86 \text{ kcal.mol}^{-1}$, while the central ring cannot be evaluated using these reactions (see Figure 6).

Finally, we have verified whether this approach can be extended to nonbenzenoid systems, so we have calculated

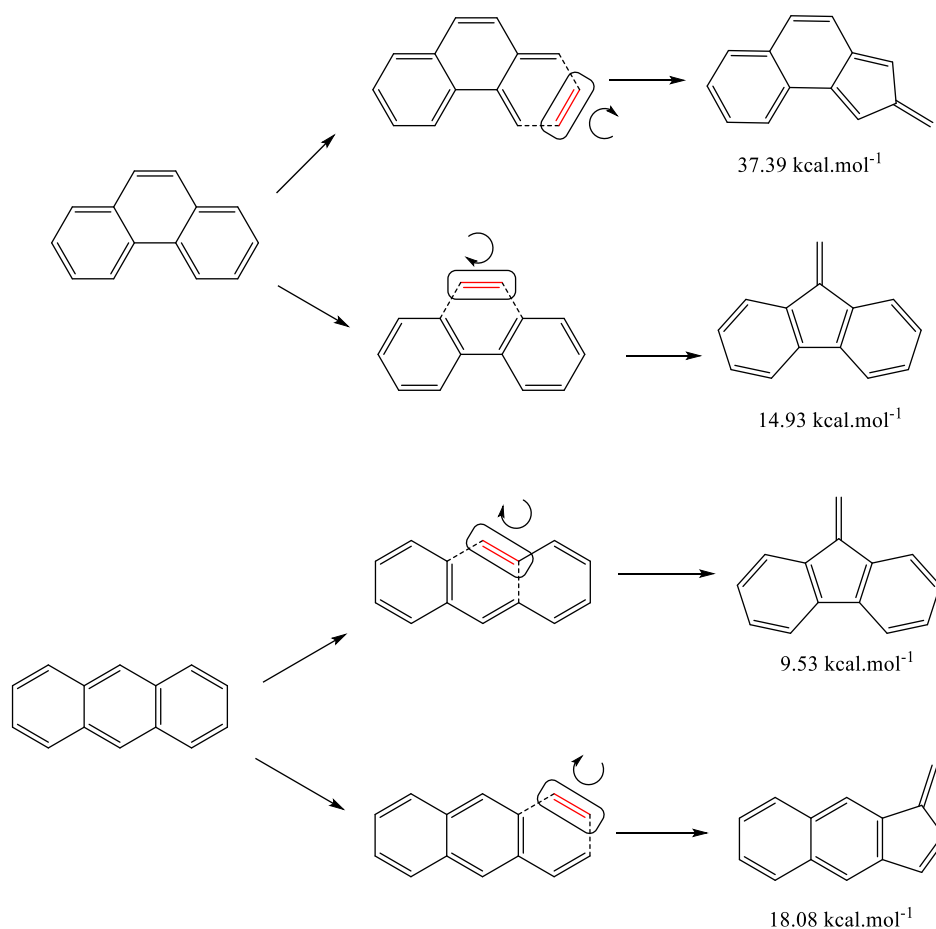


Figure 5. Fulvenization process of ISE for external local rings in phenanthrene and anthracene.

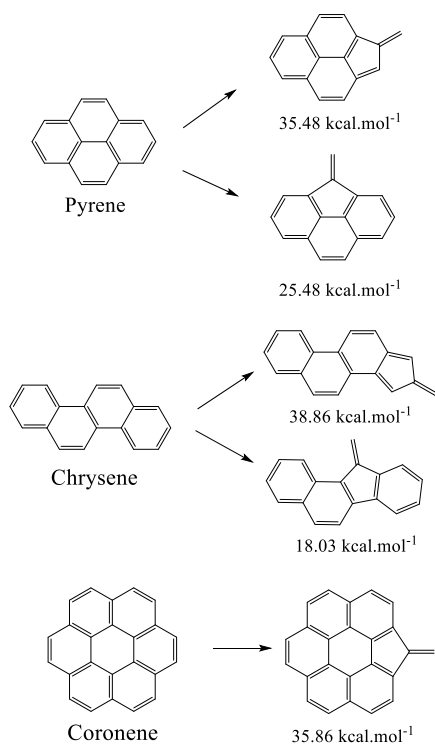


Figure 6. Fulvenization process of the ISE for the external local rings in selected polycyclic aromatic hydrocarbons.

anti(aromatic) monocycles with a formula: $C_nH_n^m$ (where $m = 1+, 0, 1-$, depending on the case). The construction of the fulvenic isomers can be seen in Figure S4. Table 1 shows the

Table 1. Isomerization Stabilization Energies Using the Fulvenization approach for (Anti)Aromatic Monocyclic Compounds Computed at the PBE0/def2-TZVP Level

$C_nH_n^m$	ISE _{Fulv}
$C_3H_3^+$	31.85
C_4H_4	-17.05
$C_5H_5^-$	66.54
$C_7H_7^+$	7.77
C_8H_8	-22.98
$C_6H_6^{2+}$	-12.02
$C_8H_8^{2-}$	23.96

values obtained at the PBE0/def2-TZVP level; for the case of the smallest system, the cyclopropenyl cation $C_3H_3^+$ with a value of 31.85 kcal.mol⁻¹ is obtained in clear agreement with its aromatic character, although the isomer used is not strictly speaking a fulvene. However, a linear molecule with the same criteria was used to construct the respective isomer. This result is consistent with previous values reported in the literature.³⁴ In the case of the C_4H_4 , $C_6H_6^{2+}$, and C_8H_8 systems, these present negative values are in agreement with their antiaromatic nature.³⁵

The value for $C_5H_5^-$ is overestimated because the corresponding isomer has contributions from the cyclo-

butadiene within its resonance forms (see Figure S5), thus causing a high instability and, consequently, a loss in planarity. For this reason, the high value includes stabilization by aromaticity and other effects related to the electronic structure of the isomer. On the other hand, the opposite is the case for the fulvenic isomer of $C_7H_7^+$, where an energy of 7.77 kcal·mol⁻¹ is obtained, similar to that reported by Dewar.³⁶ This low energy is because the $C_7H_7^+$ isomer contributes more to the aromatic resonance structure. According to calculations using natural resonance theory, the contribution percentages indicate that the aromatic resonant structures contribute 12.7%. In comparison, the nonaromatic forms have contributions of 12.10% (two of them) and 11.98% (see Figure S6). For this reason, the stabilities between the tropylium cation and its respective isomer are similar.

CONCLUSIONS

In summary, an alternative scheme for calculating aromatic stabilization energies based on the isomerization approach through fulvenic isomers has been provided. It has been applied to a wide range of systems, many of them impossible to apply under the traditional scheme proposed by Schleyer, as is the case of persubstituted benzenes and others never applied before as the inorganic analogues to benzene, Si₆H₆, and Ge₆H₆. It has been shown that it is possible to study aromaticity in biradical compounds, in both singlet and triplet states, observing the conservation of aromaticity when passing from one state to the other. It is also possible to observe the systematic reduction of aromaticity in azines not observed by using other indicators based on energetic criteria. Additionally, it has been shown that this approach allows for the differentiation of the aromaticity of local rings in different PAHs according to the most significant contributing Clar structures. Finally, for nonbenzenoid rings, it has been shown that it is possible to assign the (anti)aromatic character of various rings, except for five- and seven-membered rings, since by the nature of the fulvenic isomers, they tend to overestimate and underestimate the aromaticity of this type of rings, respectively. It has been shown that this approach does not overestimate the energies of the benzenoid rings in PAHs, unlike the traditional scheme presented by Schleyer years ago.⁶ The *fulvenization* approach is an alternative and complement for calculating aromatic stabilization energies effectively and efficiently in multiple organic systems and even in specific inorganic systems.

COMPUTATIONAL METHODS

Geometry optimizations have been carried out at the PBE0¹⁴/def2-TZVP¹⁵ level; additionally, to ensure that we have a local minimum, vibrational analyses have been performed, except for the cases of the Si₆H₆ and Ge₆H₆ systems in the *D*_{6h} symmetry and their corresponding isomers. The Gaussian16 software³⁷ package was used for the case of the biradicals, unrestricted calculations were performed, and the guess = mix command was added for the broken symmetry approach. The natural resonance theory implemented in the NBO 7.0 program³⁸ was used to compute the percentage contributions of the resonance structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c07881>.

Fulvenization process for substituted benzenes, *o*/*m*/*p*-benzynes, and inorganic benzene analogues; C_nH_n^m rings; resonance structures for fulvene isomers of cyclopentadienyl anions; and most important resonance structures for fulvenic isomers of benzene and tropylium cation (PDF)

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Notes

The authors declare no competing financial interest.

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