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The Effect of Strain on the Aromatic Character of Infinitene

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Abstract: Infinitene was synthesized in a previous study in 2021, and the molecule showed high strain energy. It was not clear how the strain affected the aromatic character of the molecule. To discuss this problem, the aromatic properties of dodecacene, [12]circulene, and infinitene have been studied. The structures of these compounds have been optimized at the DFT/B3LYP/6-311G + (d,p) level of theory, and the energy of the π orbitals has been used to determine the D' index of the aromaticity. D' for dodecacene, [12]circulene, and infinitene were 1.45, 1.45, and 1.50, respectively, showing that infinitene is an aromatic compound but with a lower aromatic character, which is in agreement with the observed strain.

Keywords: infinitene; circulene; strain effect; DFT calculations; aromaticity

Citation: D'Auria, M. The Effect of Strain on the Aromatic Character of Infinitene. *Compounds* **2023**, *3*, 336–340. https://doi.org/10.3390/compounds3020025

Academic Editors: Juan C. Mejuto and Alexander Novikov

Received: 4 January 2023
Revised: 18 March 2023
Accepted: 13 April 2023
Published: 18 April 2023

1. Introduction

Aromaticity has been one of the most important issues in organic chemistry since its foundation. The definition of aromaticity has changed over the years, from "aromatic systems are monocarbocyclic, conjugated molecules containing $(4n + 2)$ out-of-plane π electrons" to "cyclic systems having a large resonance energy in which all the atoms in the ring take part in a single conjugated system" and finally to "cyclic diatropic systems with a positive calculated Dewar RE in which all the ring atoms are involved in a single conjugated system" [1]. More recently, commonly used aromaticity rules have been subjected to a significant revision showing the limitations of the proposed approaches [2,3]. Several approaches have been used in order to determine the aromatic character of a compound, including empirical resonance energy (ERE), aromatic stabilization energy (ASE), bird index, harmonic oscillator model of aromaticity (HOMA), and nucleus-independent chemical shift (NICS), all of which have been proposed [4–14]. An important role in the evaluation of the aromatic character was played by the strain effect in tested compounds [15–17].

Some aromatic indices failed in our estimation on the strain in an aromatic compound. For example, in the case of the compounds **1** and **2** (Figure 1), where **2** did not show a planar structure, HOMHED (harmonic oscillator model of heterocyclic electron delocalization) [18] is the same (0.88) for both compounds, while D' index [19] presented 1.40 for **1** and 1.45 for the compound **2**, showing that **1** is more aromatic than **2**.

D' index (Equation (1)) is the evolution of a previously reported aromatic index [20] and it is an index related to the energy of occupied π orbitals.

$[\pi_1 + \sum_2^n(\pi_1 - \pi_n)]_0$ represents the energy difference between the π orbitals for the parent compound (benzene), while $\pi_1 + \sum_2^n(\pi_1 - \pi_n)$ is the same value for a generic aromatic compound. a_0 is the number of atoms in the molecule participating in the formation of π orbitals in the reference compound, and a is the number of atoms in the molecule participating in the formation of π orbitals in the tested molecule.

$$D' = \left\{ \frac{[\pi_1 + \sum_2^n(\pi_1 - \pi_n)]_0}{\pi_1 + \sum_2^n(\pi_1 - \pi_n)} \right\} \times \frac{a}{a_0} \quad (1)$$

Recently, infinitene **3** (Figure 2) was synthesized [21], and this compound showed a large strain energy (60.2 kcal mol^{-1}) (on the origin of name cfr. [22]). NICS determination

showed a benzenoid ring with a good aromatic character as well as other rings with very low aromatic values. The Möbius rule for twisted annulene was in agreement for a non-aromatic compound. However, calculations are in agreement with an aromatic compound [23]. The spectroscopic properties, such as excited state dynamics, of infinitene have been reported [24–26].

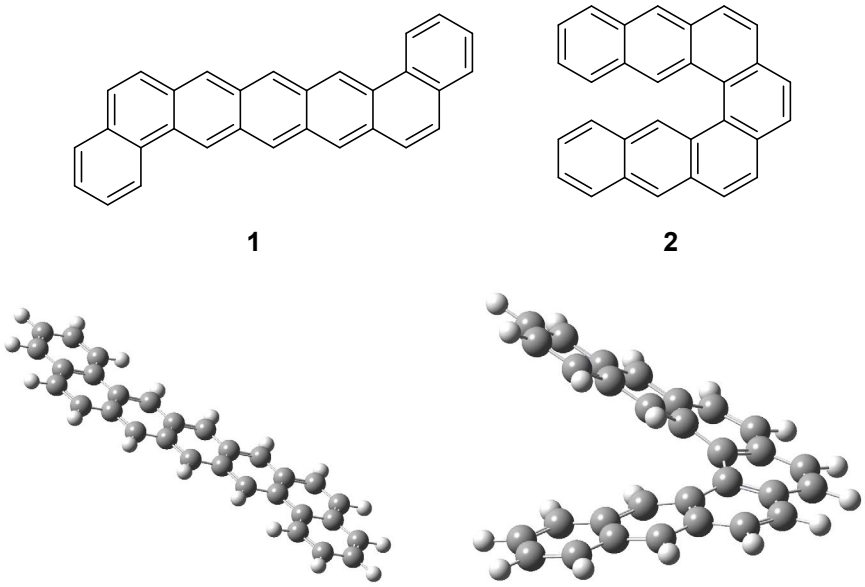

Figure 1. Compounds **1** and **2**.

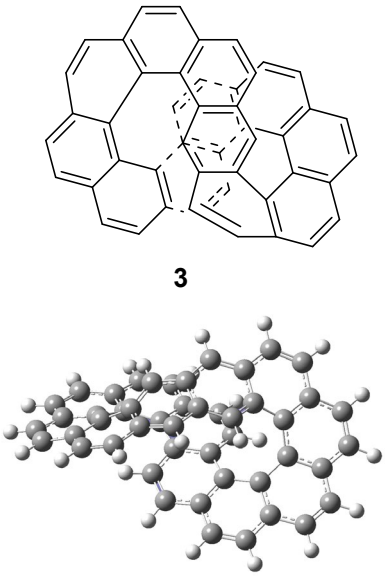

Figure 2. Infinitene **3**.

In this article, we present our results on the calculation of the aromaticity on infinitene with the aim to provide an estimation of the effect of strain considering linear twelve condensed aromatic ring, dodecacene, cyclic [12]circulene (Figure 3) and [12]infinitene.

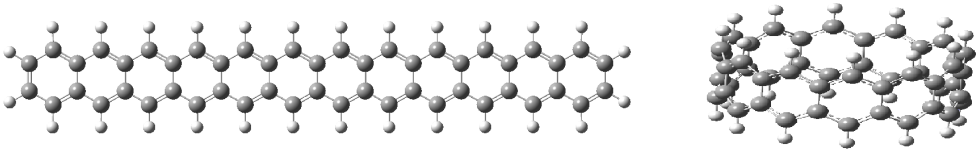

Figure 3. Dodecacene (**left**) and [12]circulene (**right**).

2. Materials and Methods

Gaussian09 has been used for the discussion of computed geometries [27]. All the computations (Supplementary Materials) were based on the density functional theory (DFT) [28] by using the B3LYP hybrid xc functional [29]. Geometry optimizations from the Gaussian09 program have been obtained at the B3LYP/6-311G + (d,p) level of approximation. Geometry optimizations were performed with default settings on geometry convergence (gradients and displacements), integration grid, and electronic density (SCF) convergence. Redundant coordinates were used for the geometry optimization as produced by the Gaussian09 program. Analytical evaluation of the energy second derivative matrix with respect to Cartesian coordinates (Hessian matrix) at the B3LYP/6-31G + (d,p) level of approximation confirmed the nature of minima on the energy surface points associated with the optimized structures.

3. Results and Discussion

Calculations in order to optimize the structures have been performed at the DFT/B3LYP/6-311G + (d,p) level of theory. Figure 4 presents the HOMOs and LUMOs of dodecacene, [12]circulene, and infinitene.

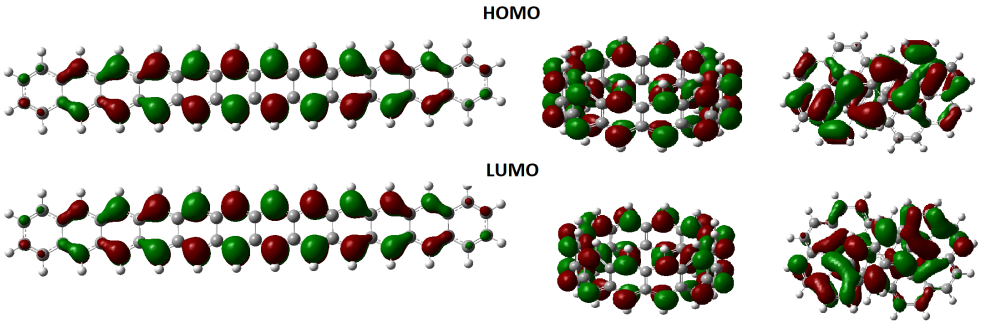

Figure 4. HOMOs and LUMOs of dodecacene (**left**), [12]circulene (**center**), infinitene (**right**).

It is noteworthy that the HOMO and LUMO of infinitene do not correspond to those reported in a previous article, where the structures were optimized at the PBEO/6-311G + (d,p) level of theory [21]. The optimized structure performing TD calculations obtained at the DFT/B3LYP/6-311G + (d,p) level confirmed the observed differences. An attempt to use the PBEO functional used in calculations did not modify the observed differences. Table 1 presents the energy of π orbitals. These values were used to calculate the D' index as reported in Equation (1).

Table 1. Energy of π orbitals of dodecacene, [12]circulene, and infinitene [eV].

Orbital	Dodecacene	[12]Circulene	Infinitene
π_1	−11.34	−11.66	−11.10
π_2	−11.23	−11.58	−11.03
π_3	−11.05	−11.58	−10.44
π_4	−10.80	−11.42	−9.74
π_5	−10.48	−11.42	−9.68
π_6	−10.10	−10.99	−9.23
π_7	−9.66	−10.99	−9.13
π_8	−9.15	−8.97	−9.04
π_9	−8.73	−8.79	−8.76
π_{10}	−8.60	−8.79	−8.51
π_{11}	−8.60	−8.79	−8.24
π_{12}	−8.40	−8.79	−8.16
π_{13}	−8.14	−8.25	−7.91
π_{14}	−8.00	−8.25	−7.83
π_{15}	−7.56	−7.45	−7.30
π_{16}	−7.42	−7.45	−7.17
π_{17}	−7.38	−7.38	−7.00
π_{18}	−6.95	−6.47	−6.91
π_{19}	−6.48	−6.18	−6.18
π_{20}	−6.46	−6.18	−6.18
π_{21}	−6.43	−4.70	−5.88
π_{22}	−5.85	−4.70	−5.68
π_{23}	−5.23	−4.32	−5.47
π_{24}	−4.59	−11.66	−5.05
π_{25}	−4.01		
D'	**1.45**	**1.45**	**1.50**

On the basis of the energy of π orbitals, it is possible to calculate the value of D' (Table 1). Dodecacene and [12]circulene showed the same value, 1.45, while infinitene showed a value of 1.50. Based on these results, we are able to make the following considerations: (1) all the compounds are aromatics; (2) the large ring present in [12]circulene does not alter the aromatic character of the molecule; (3) the large strain present in the molecule can modify the aromatic character and the molecule shows a lower aromatic character; and (4) the difference between 1.45 and 1.50 accounted for the lower aromatic character.

4. Conclusions

The results described above showed that D' index can be used in order to determine the aromatic character of strained molecules. We have shown that infinitene is an aromatic compound, which is in agreement with another computational work [23], but its strained structure reduces the aromaticity of the molecule. At the moment, the aromaticity of infinitene is similar to that of [6]annulene, a very strained molecule [19].

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/compounds3020025/s1, DFT energies and xyz coordinates for optimized structures.

Funding: This research received no external funding.

Data Availability Statement: Available data can be found in the Supplementary Materials of this article.

Conflicts of Interest: The author declares no conflict of interest.

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