

Homodesmotic reactions in helicene and phenacene molecules

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Helicene molecules were analysed on the basis of their intrinsic aromaticity, and compared with the corresponding phenacene. The analysis of aromaticity was performed by homodesmotic reactions, and by the nucleus independent chemical shifts (NICS) index in the centre of the aromatic rings as well as in the centre of the helix. The results are very interesting, because the NICS shows that there is a strong antiaromatic zone in the centre of the molecule, and a strong aromatic zone in the strip. Therefore, these molecules represent a medley of electronic effects.

Keywords: Aromaticity; Homodesmotic reactions; Delocalisation index

1. Introduction

The first helicene molecule, a heterocycle was prepared in 1903 [1]. Thirty years later, the first homocycle helicene was synthesised [2]. However, for many years, these molecules were considered only beautiful structures with no utility, until research was carried out in which new and interesting applications were established.

The growing number of ortho-fused aromatic rings causes nonbonded repulsions between their faces, and this forces the molecule to adopt the characteristic cylindrical spiral structure [3]. Some methods have been developed for the preparation of helicenes functionalised with reactive groups, by combining enol ethers of diacetyl aromatic species with *p*-benzoquinone [4–6]. In addition, Vollhardt *et al.* recently produced the first helical phenylene [7,8].

The idea that helicenes might stack into long columns in the liquid phase, in solution or as solids, and that the columns of non-racemic helicenes could twist into large corkscrew configurations, transforms helicenes into useful molecules. Another application of helicenes might be in asymmetric catalysis [9,10].

Some examples of helicenes have shown long fibrous morphology, large circular dichroisms, and specific rotations. Others exhibited a large second-order non-linear response [11].

These features of the helicenes, together with their electronic properties [9,12], are related to their inherent

chirality [13], and may also be related to the aromatic character of the molecules.

In the theoretical field, Poater, Solà *et al.* [14], conducted a study with a view to analysing the local aromaticity of the series of [*n*]acenes, [*n*]phenacenes, and [*n*]helicenes, *n* = 1–9, using three methods: an indicator of aromaticity based on electron delocalisation, PDI; another based on structure, HOMA; and a third one based on magnetic properties, nucleus independent chemical shifts (NICS). They showed that for the [*n*]acene series, the inner rings are more aromatic than the outer rings, although the former are more reactive. For the [*n*]phenacene series, they showed that the most external ring is also the most aromatic, and that there is a damped alternation of the local aromaticity from the outer to the inner ring. Finally, they determined a small change in the aromaticity between the [*n*]helicenes and [*n*]phenacenes; the [*n*]phenacenes being slightly more aromatic than their helicene isomers.

In the present work, the aromaticity is again studied, however, the main interest is now centred on the energy differences, produced as a result of the aromaticity, which are related to the change of shape, implying strong differences in the behaviour of helicenes with respect to their phenacene isomers. Therefore, in this case, homodesmotic reactions were implemented in order to address these differences. Furthermore, an NICS [15] study was performed in other zones, as well as an examination of the DI mean value, which is similar to the PDI index [16]; this

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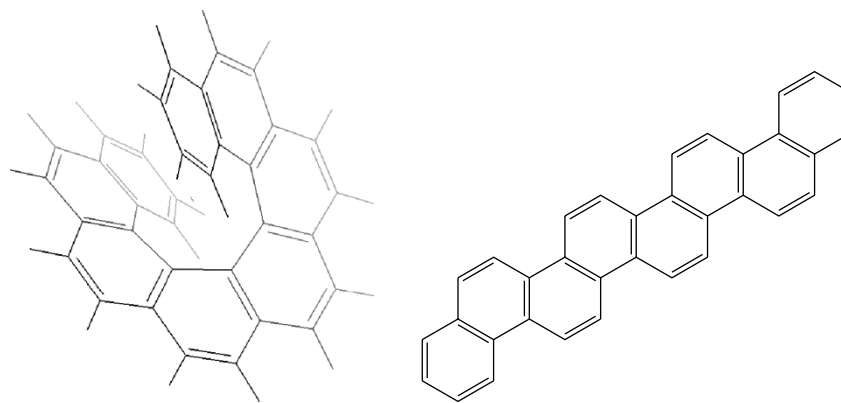


Figure 1. Molecules under study.

last being based on the atoms in molecules model [17] applied to the molecules under study. This analysis was carried out in order to look for magnetic effects related to the spiral shape of these molecules.

2. Methods

All structures were optimised in the gas phase, using the Jaguar 4.0 package [18]. A pure DFT method, containing Becke's gradient correction [19] for exchange and Perdew–Wang's for correlation [20], was used for energy evaluations. All calculations were performed using the 6–31G** basis set. Frequency calculations were carried out at the same level of theory, in order to confirm that the optimised structures were found to be at the minimum of the potential surface. These frequencies were then used to evaluate the zero-point vibrational energy, the thermal vibrational corrections to the enthalpy, and the total enthalpy values.

We calculated the DI, as described in the theory of atoms in molecules [17]. For this purpose we use the pair density index calculated by the Hartree–Fock approximation at the level of theory indicated above. To obtain the values of the DI we employed the AIM-PAC program [17h]. NICS15 is a technique that was proposed by Schleyer as a new aromaticity index. The authors call it absolute magnetic shielding and compute the value at the ring

centres, which are determined by the non-weighted mean of the heavy atom coordinates. In this work, NICS calculations were performed following this technique, the conditions for these calculations were Gaussian03 [21] at 6–31 + G** level.

3. Results and discussion

The kinds of compounds that represent the subject of the present study are shown in figure 1. The study was carried out on molecules containing six, seven and eight aromatic rings on their corresponding strips; the molecules shown in figure 1 represent only some examples of all the molecules studied.

The global aromaticity of all molecules was estimated by means of the calculation of aromatic stabilization energy (ASE; by the homodesmotic reactions method), whereas local aromaticity was calculated in defined zones of the molecules (helicenes only) by means NICS and DI methods. This scheme allows us to obtain a good overview of the aromaticity in a specific species.

The general form of the homodesmotic reaction is shown in figure 2. The reactive molecule is tetra(vinyl-ethylene) (TVE), a very versatile species due to its containing tertiary as well as quaternary carbon atoms, both containing double bonds, which are the kind of fragments useful for building

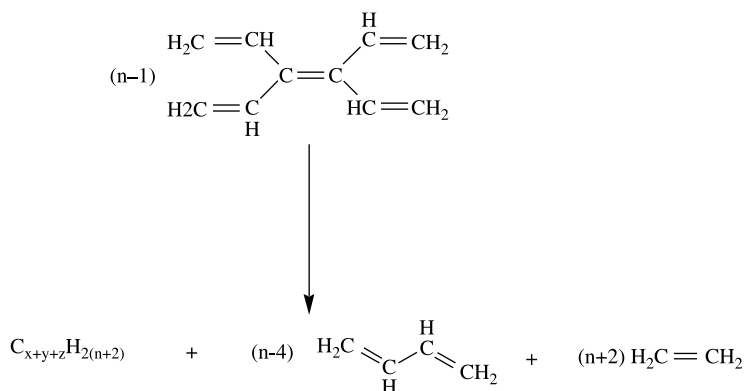


Figure 2. Model homodesmotic reaction. Where: $x = 2(n + 2)$; $y = (n - 4)$; $z = (n + 2)$ and n is the number of cycles that are contained in the strip of the respective molecules.

Table 1. ASE of helicene and phenacene molecules.

Molecule	Energy (kcal/mol)	Molecule	Energy (kcal/mol)	Difference
[6]helicene	-153.3550	[6]phenacene	-171.8012	-18.4462
[7]helicene	-177.1589	[7]phenacene	-201.2678	-24.1089
[8]helicene	-200.7664	[8]phenacene	-231.0845	-30.3181

poly-aromatic hydrocarbons that contain ring fusions. This reactive molecule was suggested by George *et al.* [22], who have provided the main contribution to the study of aromaticity by this method [23].

The results obtained by the homodesmotic reactions correspond well with the earlier, similar study by Schulman and Disch [24], in which a homodesmotic reaction, based solely on the same phenacene and helicene molecules with a different number of aromatic rings (without consideration of other molecules as a source of tertiary and quaternary carbon atoms), yields an approximate value of 6.2 kcal/mol, as the difference between the two isomers (helicenes and phenacenes of the same molecular weight), favouring the phenacenes.

A comparison of the enthalpy values that represent the ASE of helicene and phenacene is shown in Table 1.

The difference outlined in the last column shows that phenacene molecules present significantly more aromatic character than helicenes. It is necessary to note that the value of 6.2 kcal/mol, suggested by Schulman and Disch, represents, in this particular case, the increase in the energetic difference that accompanies each increase in molecule size in each aromatic ring. Therefore, each phenacene molecule gains this quantity over its corresponding isomer (helicene) with each new aromatic ring that is joined to the chain.

The first estimation of the aromaticity of these molecules (in both isomer shapes) was carried out by Portella, taking advantage of the NICS [15], the HOMA [25] and the PDI methods. However, in our case, the NICS index was calculated at the centre of the tunnel formed by the spiral, i.e. a dumb atom was placed on the C2 axis that passes through the centre of the formed helix, as shown in figure 3. Here, it is important to note that the dumb atom was positioned in a zone that is not confined as in the case of a single ring, therefore, in this case it is convenient to consider the result as a global estimation of aromaticity. The result is very interesting, since the value indicates antiaromaticity for the three helicene molecules studied, as can be seen in Table 2.

Portella found that NICS is a poor method of estimating the aromaticity in helicenes, because there is a super-estimation of the index compared to the same obtained by HOMA [25]. This feature is related to the effect of magnetic coupling brought about in the external rings when they are so close as to superimpose their molecular orbitals. The result outlined here seems to confirm the large result obtained by Portella, since a large magnetic field is yielded by the sum of the small magnetic fields of each ring, which generates a large spiral on the exterior of the molecule, very different from the interior, where the

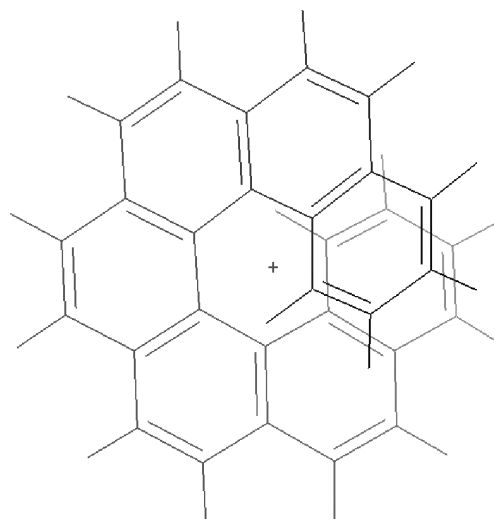


Figure 3. The dot represents the position in which the NICS index was estimated.

Table 2. NICS value in the central channel of helicene molecules.

Molecule (rings)	NICS
6	7.2808
7	7.4598
8	7.8497

antiaromatic region is located, and which appears to possess a very poor electronic density.

The DI was calculated by taking the centre of the helicene molecules as a six-membered ring, in order to evaluate the electronically-poor region mentioned above. The procedure consists in calculating a mean value for the DI of the *para*-related carbon atoms. The *para*-related atoms for [7]helicene, from figure 4, are:

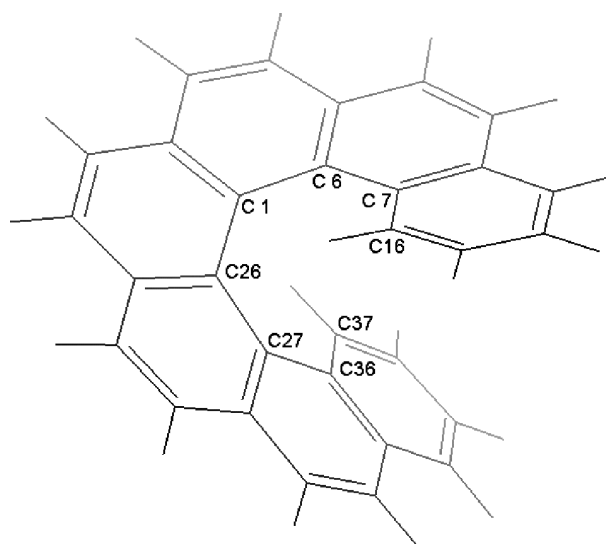
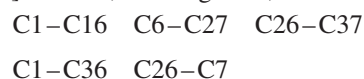


Figure 4. DI mean value results for the central channel of the [7]helicene molecule. The values were obtained for the *para*-related carbon atoms outlined earlier.

Table 3. DI value for helicene molecules.

Molecule	DI mean value
[6]helicene	0.01331
[7]helicene	0.01199

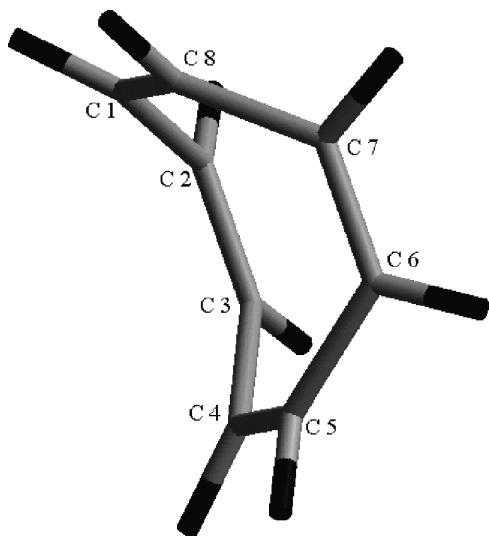
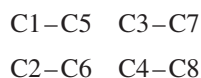


Figure 5. COT in tub shape. The numeration of the carbon atoms corresponds to the DI mean value relationships used in the estimation.

The DI mean value for the two molecules is very small (Table 3) compared with the PDI value obtained for benzene, 0.1039, which means that the electrons delocalised in the centre of the helicenes are too few for this region to be considered aromatic. Indeed, it appears that there is no electronic flow in this position, and this result confirms that the central channel has no intrinsic electronic current.

We also calculated the DI for the cyclooctatetraene (COT), a well-known antiaromatic molecule, as a reference for our non-aromatic DI mean value for the central region of the helicenes. The geometry used was the tub-shaped one (figure 5). The DI mean value for COT was 0.01397 in the tub shape and 7.736×10^{-3} for the planar one, and was obtained for the following relation of carbon atoms:



The DI criterion considers as a reference the carbon atom placed at the *para* position. In our case we follow a similar criterion analyzing each carbon atom taking as a reference the opposite carbon (not the *para* position) because the geometry of COT does not allow the same topology as in a six member ring. This DI criterion has not been applied to molecules other than six-member rings, therefore we carried out other kinds of calculation in order to validate this last result. This new calculation consists in carry out the same analysis on $\text{C}_8\text{H}_8^{+2}$, an eight member aromatic ring species, the result is satisfactory since the same relation yields an average value of 0.056 for this ion indicating medium aromaticity, and this result is

comparable to the first ring of naphthalene (0.055) or the second ring of crysene (0.052) [27].

The analogy between the results obtained with the helicene molecules and those of the COT is direct. COT has been considered an antiaromatic molecule in planar form and not aromatic at all in the tub shape [26] in the absence of ionic charges. Therefore, considering the similarity between both DI values, we concluded that the channel of helicene molecules is non-aromatic under this criterion.

The results obtained with the FLU [27] index for central channel in the hexahelicene, heptahelicene and octahelicene agree with those obtained with the NICS and the DI; however, the index was developed for cyclic molecules and the central region of the molecules we have studied certainly are not a closed species. The results of the topological analysis from the theory of atoms in molecules, show a critical point and a bond path between the carbon atoms that are in both internal extremes of the helical chain, but only for the hexahelicene molecule. Thus, we may consider that the central channel of the hexahelicene is a cycle and use the FLU index only for this molecule, giving a value of 0.208 in the central channel; indicating anti-aromaticity for this case. Furthermore, the FLU index for the individual rings of hexahelicene are 0.024 for the first ring, 0.061 for the second ring and 0.056 for the third ring counting from the edge to centre of the chain. These results agree with the analysis made using the PDI index indicating a more aromatic character at the edge of the helicene molecules.

4. Conclusions

The aromaticity of helicene and phenacene molecules was evaluated from an energy point of view. Our results confirm those obtained by other authors, i.e. that phenacenes are more aromatic than their corresponding isomers, the helicenes. One of the reasons for this behaviour is that helicene molecules generate a region of antiaromaticity, i.e. the central channel of helicenes was evaluated and found to exhibit an anti-aromatic behaviour (or not-aromatic depending on the corresponding method used in each evaluation). This feature contributes to the lower stability of helicene in comparison with their analogues.

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