

Ab initio and DFT study of the aromaticity of some Fulvalenes derived from Methylidenecyclopropabenzene

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Received: 1 February 2007 / Accepted: 24 April 2007 / Published online: 2 June 2007
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Abstract Methylidenecyclopropabenzene (MCPB) **1** and Fulvalenes **2–4** are molecules of special interest due to the relation between structure and aromaticity. The aim of this work was to analyze this relation and to quantify the aromaticity in **1–4** using different methods. Magnetic properties are directly related with aromaticity; here we studied the magnetic susceptibility and the anisotropy of the magnetic susceptibility. Nucleus independent chemical shift (NICS) and the anisotropy of the induced current density (ACID) were also employed. Tools of very different nature, geometric indexes HOMA and Bird, were determined too for **1–4**. All of these measures were found to be in agreement.

Keywords Aromaticity · Fulvalenes · Magnetic properties

Introduction

Fulvenes and Fulvalenes are conjugated rings connected with an exocyclic double bond. The synthesis of these reactive molecules is of special interest due to the relations between structure and aromaticity [1]. Cyclopropabenzene (see Fig. 1) is the simplest member of ortho bridged

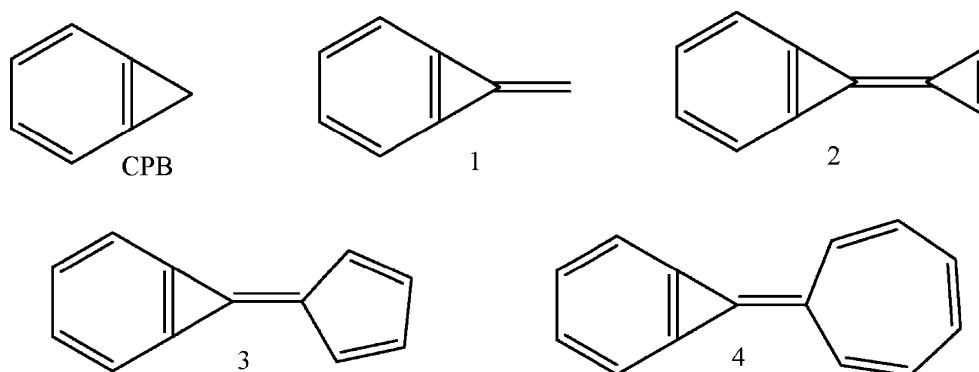
aromatic molecules. A similar molecule, methylidenecyclopropabenzene (MCPB, **1**) may be considered as a benzanulated triafulvene and an unusual radialene, due to the possible resonant structures. The fulvalenes **2–4** can be obtained as derivatives from MCPB, just adding a carbocycle that contains an odd number of carbon atoms [2a,b]. Apeloig et al. [3] performed HF/STO-3G calculations of these not synthesized yet molecules and observed a considerable polarization of π -electrons, since there is an important contribution of resonant structures that have a partial positive charge in the cyclopropabenzene (CPB) fragment for molecules **3** and **4**, and a partial negative charge in the same fragment for molecule **2**. For this reason, dipolar moment has opposite sign in **2** with regard to those of **1**, **3** and **4**. Later, structures **1–4** were optimized at the HF/6-31G(d,p) and MP2(fc)/6-31G(d,p) levels by Apeloig and co-workers [4], in order to consider the electronic correlation.

The aim of this work is the quantification of the aromaticity of these molecules. In general, an aromatic compound has a cyclic and conjugated set of p orbitals that constitute the π -system. The number of π -electrons is $4n+2$, where n is a whole number: this fact is known as the Hückel rule. Due to the resonance energy, they have an unusual thermodynamic stability, but the essential feature of this kind of compounds is its magnetic behaviour. Magnetism and aromaticity are directly associated concepts: due to the ring current generated by the delocalized π -electrons, aromatic molecules are strongly diamagnetic. In presence of an external magnetic field they develop another magnetic field perpendicular to the plane that contains the current-, that flows in the opposite way to the external one. Aromatic compounds have a very high negative magnetic susceptibility, and the antiaromatic ones have a very high positive magnetic susceptibility. Anisotropy of magnetic susceptibility has the same trend. Schleyer and Jiao [5] have

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Fig. 1 Cyclopropabenzene (CPB), Methylidencyclopropabenzene (MCPB) **1** and the derivated fulvalenes (**2**, **3** and **4**)



defined aromatic compounds as “*compounds which exhibit significantly exalted diamagnetic susceptibility (...). Cyclic electron delocalization also may result in bond length equalization, abnormal chemical shifts and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilization. Those compounds with exalted paramagnetic susceptibility may be antiaromatic*”.

There are two ways to quantify the aromaticity: *locally* (in a point, in a concrete region of the space, in a cycle...) or *globally*, i.e., considering the whole molecule. Magnetic susceptibility and anisotropy of magnetic susceptibility are global measures. They give us an idea of *how aromatic* is a molecule. On the other hand, “nucleus independent chemical shift” (NICS), introduced by Schleyer [6] and directly related to the chemical shift in vacuum, is another useful tool to quantify aromaticity. It has a local character, since it is calculated in a specific point. Anisotropy of the induced current density (ACID) is another method that uses the magnetic properties, developed by Herges and Geuenich [7]. This powerful tool has been used for the quantitative study of delocalization in molecules. Aromaticity measures based on geometric indexes are inspired in the trend of aromatic compounds of making equal the distances of the bonds in an aromatic ring. There are many different geometric indexes; here we have used two of them, Bird and HOMA indexes [8], to evaluate the aromaticity in the benzene rings of the molecules **1–4**. The greater the index value is, the larger aromaticity we have. Both indexes have a local character since they only allows us to calculate the single-ring aromaticity. In the present paper we use all these methods with molecules **1–4**.

Computational methods

In the present work, the geometry of each molecule was fully optimized using the Gaussian 98 software package [9] with the 6–31G(d,p) basis set and density functional theory (B3LYP functional) [10]. All points were characterized as minima by calculating the harmonic vibrational frequencies by using analytical second derivatives.

Magnetic susceptibility values were calculated by computing the NMR shielding tensors using the CSGT method [11].

We also carried out ACID calculations with the program supplied by Herges [7]. ACID is a scalar field and it represents the delocalized electrons’ density, not the total electron density. Plotting isosurfaces of ACID, we can know how strong the delocalized ring currents are. Furthermore, we can find out the sense of turn of these currents if we project the density current vectors on the isosurfaces: if the current flows under the left hand rule, it is a diatropic current; if it flows in the opposite sense, then we have a paratropic current. The anisotropy can be obtained calculating the density current tensor, using the CSGT method performed by Keith and Bader.

NICS [6] values were calculated employing the CSGT method as well. When an external magnetic field is applied, an internal one appears. The tensor that relates them is σ , known as the *shielding tensor*. Using the Biot-Savart law, σ can be obtained directly from the current density. The shielding constant is the isotropic value σ , which is 1/3 of the shielding tensor’s trace. NICS will be that value with a sign change, and this is just the chemical shift in vacuum.

Bird [8c] index takes values from 0 to 100, where benzene is the maximum value of the aromaticity scale, 100. HOMA [8a,b] takes values from 0 to 1. It is important to emphasize that benzene has not HOMA=1.

Results and discussion

1. Geometries, energies, dipole moments and NBO charges. First, we reproduced the MP2 calculations performed in the previous work mentioned above [4]. The geometries obtained were used as starting point for the optimization with B3LYP and 6–31G(d,p) basis set. Molecules **1–4** were fixed with C_{2v} symmetry [12]. Electronic energies are showed in Table 1. The geometries obtained with DFT are very close to MP2 geometries of Apeloig et al. [4]. Benzene values were used as reference. In the table we can see the dipolar moments too. Benzene is an apolar substance, but **1**, **2**,

Table 1 Electronic energies, electronic energies including the zero-point energy correction and dipole moments

	E_{el} (a.u.)	$E_{el} + ZPE$ (a.u.)	μ (D)
1	-308.35126	-308.24180	1.419
2	-384.45533	-384.33694	2.455
3	-461.96582	-461.80977	3.286
4	-539.37649	-539.18567	0.280

3 and **4** have a significant dipolar moment value. This is the expected behaviour, considering the predominant resonant structures commented in the introduction. Only **4** has a dipolar moment near to zero. It is important to note that **2** has the dipolar moment in opposite sense of **1**, **3** and **4**, because this is the only one that does not have a resonant structure with partial positive charge over the CPB fragment. The fact that **4** has resonant forms with similar importance of CPB charged negatively and positively is traduced in its small apolarity. To confirm those facts, we calculated the NBO charges of **1–4** and the results can be viewed in Table 2. We divided each molecule in two fragments: the CPB and the remaining ring. The charges of the atoms of the two fragments for each molecule were added. In a qualitative way we observe that in **1**, CPB has a partial positive charge of +0.026; in **3** and **4**, CPB fragment has +0.200 and +0.006 values, respectively. This very small value (+0.006) explains why **4** has a close to zero dipolar moment. In contrast, in **2** we find a value of -0.157.

The CPB fragment geometries are similar for all molecules; maybe the most significant difference corresponds to the double bond between conjugated rings, because it shows remarkable changes from **1** to **4** (1.334, 1.325, 1.356 and 1.365 Å for **1**, **2**, **3** and **4**,

Table 2 NBO charges in **1–4**

	1	2	3	4
C1	-0.028	-0.047	-0.116	-0.134
C2	-0.018	-0.125	0.076	-0.014
C3	0.002	0.015	0.021	0.018
C4	0.002	0.015	0.021	0.018
C5	0.002	-0.031	0.009	-0.022
C6	0.002	-0.031	0.009	-0.022
C7	0.018	0.000	0.032	0.014
C8	0.018	0.000	0.032	0.014
C9		0.103	-0.023	0.075
C10		0.103	-0.023	0.075
C11			-0.020	-0.022
C12			-0.020	-0.022
C13				0.011
C14				0.011

Charges of the hydrogens bonded to each carbon atom were added

Table 3 Magnetic susceptibility (χ) and the anisotropy of the magnetic susceptibility (χ_{anis})

	χ (cgs-ppm)	χ_{anis} (cgs-ppm)
Benzene	-48.13	-119.36
1	-56.10	-126.45
2	-63.20	-150.85
3	-75.56	-193.60
4	-64.53	-141.74

respectively). The decrease in this distance in **2** is directly related with the weight of the resonant structures we commented above.

2. Aromaticity measures.

Magnetic susceptibility and anisotropy of the magnetic susceptibility. The magnetic susceptibility (χ) and the anisotropy of the magnetic susceptibility (χ_{anis}) are shown in Table 3. The most obvious conclusion that can be drawn from these results is that all the studied molecules are highly aromatic, because their χ values are very negative. The second important conclusion is that all of them are more aromatic than benzene.

We can see that aromaticity increases from **1** to **3**. **4** does not follow the trend: as we will later see, this molecule has a clearly antiaromatic seven-member cycle, and therefore a smaller aromaticity global value. The χ_{anis} values follow the same trend, and the agreement between χ and χ_{anis} is almost complete; the only difference is the position in the order of aromaticity of **4**.

Nucleus independent chemical shift (NICS) It is well-known that negative NICS values are usually associated to aromaticity, whereas positive values denote an antiaromatic behaviour. Three types of measures of NICS were

Table 4 NICS (in ppm) calculated in the centre of: (a) benzene ring; (b) cyclopropane ring of the CPB fragment; (c) the carbocycle of odd number of atoms

	(a)	(b)	(c)
NICS ^(a) (0)			
Benzene	-11.57		
1	-9.38	-21.56	
2	-9.00	-18.57	-25.71
3	-8.64	-23.21	-5.79
4	-9.12	-23.00	+11.28
NICS ^(b) (1)			
Benzene	-12.86		
1	-12.19	-10.16	
2	-11.21	-6.32	-8.12
3	-11.79	-10.93	-6.37
4	-11.75	-9.73	+6.89

^(a) NICS (0) is NICS calculated in the plane of the molecule. ^(b) NICS (1) is NICS calculated at 1 Å of distance from the plane.

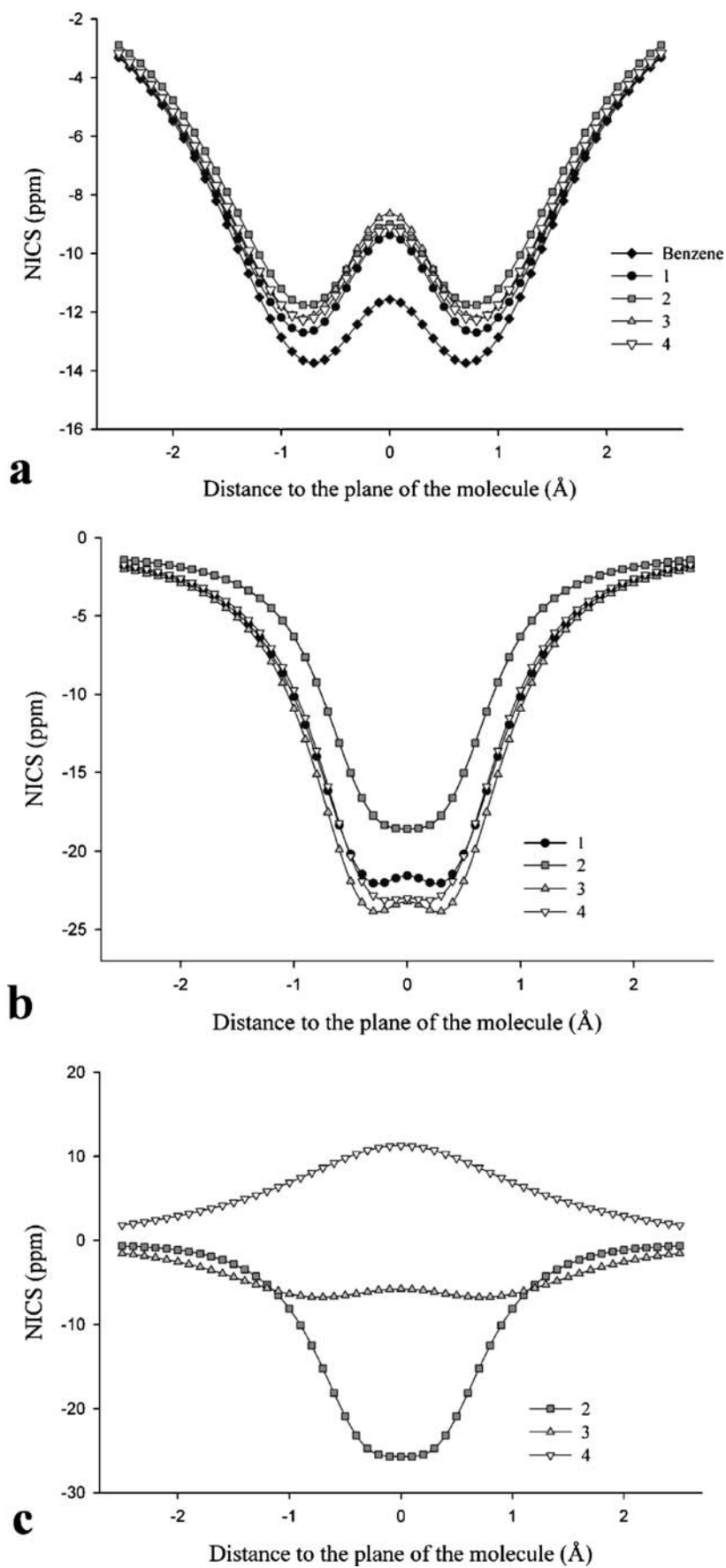


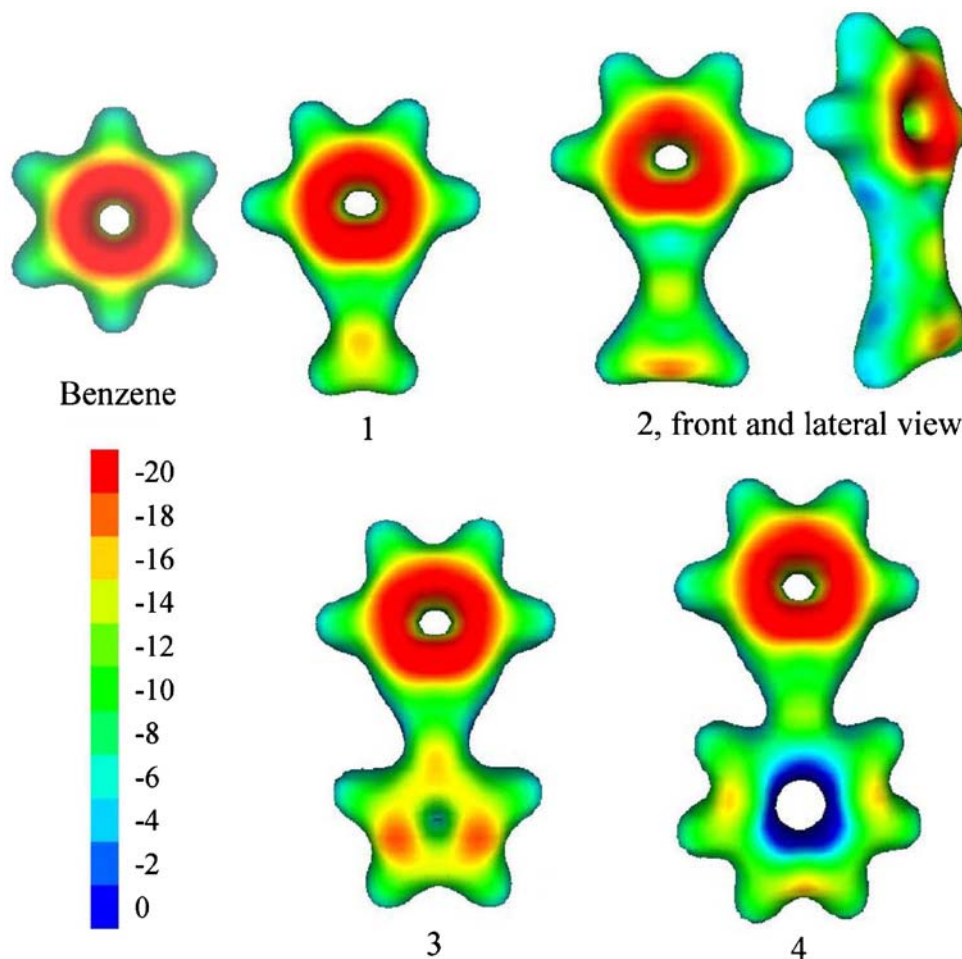
Fig. 2 NICS calculated along the axis: (a) benzene ring; (b) cyclopropene ring of CPB fragment; (c) cycloheptatriene, cyclopentadiene and cyclopropene ring, the additional carbocycles of an odd number of atoms

performed: in a point, along an axis and in a three dimensional grid around the molecule. For the first option we chose the geometrical centres of the different rings of each molecule: one in the molecule's (NICS(0)), and one at 1 Å distance from the plane (NICS(1)) [13]. As Table 4 shows, we can check that the high global aromaticity of 1–4 is not due to the benzene ring. In fact, this cycle's NICS values are lower than the benzene's NICS values. It is also important to note that the difference between the benzene molecule and the benzene ring of 1–4 is not as large in NICS(1) as in NICS(0). The reason is that NICS(0) overestimates aromaticity, since we are measuring in the molecule's plane, where we have an important influence of the electrons of C–C and C–H σ -bonds. If we want to evaluate the contribution of π -orbitals (the really important one for aromaticity) it is much more meaningful to observe the NICS(1) values. The NICS values for points (b) and (c) are useful to show that these points have the larger contribution to the global aromaticity. At first glance, the

cyclopropane of the CPB fragment is the one that makes the most important contribution. However, we said previously that NICS(0) remarkably overestimates aromaticity, and that NICS(1) values are much lower in that cycle. In conclusion, (c) is the main differential factor between the studied molecules. While 2 and 3 have a third aromatic ring, 4 presents positive values of NICS (+11.28 in the plane, +6.89 at 1 Å) that explain the decreasing of the global aromaticity in this molecule.

We also studied how NICS changes along a perpendicular axis to the molecule's plane, crossing the ring centres (see Fig. 2, (a), (b) and (c)). Once more, benzene values are offered as reference. In the benzene rings NICS takes negative values, where the minimum is not in the molecule's plane, but at 0.8 Å of distance from the plane. That means that the region of larger aromaticity coincides with the π -region [12]. In contrast, the cyclopropane ring of CPB has a very negative minimum within the plane, and then, NICS increases quickly, showing that this ring is not so aromatic as we could think. Finally, the ring that makes different the fulvene 1 and the fulvalenes 2, 3 and 4 has various shapes according to the specific case. While cyclopropene of 2 is similar to the cyclopropane ring of

Fig. 3 Spatial NICS over an isosurface of electron density

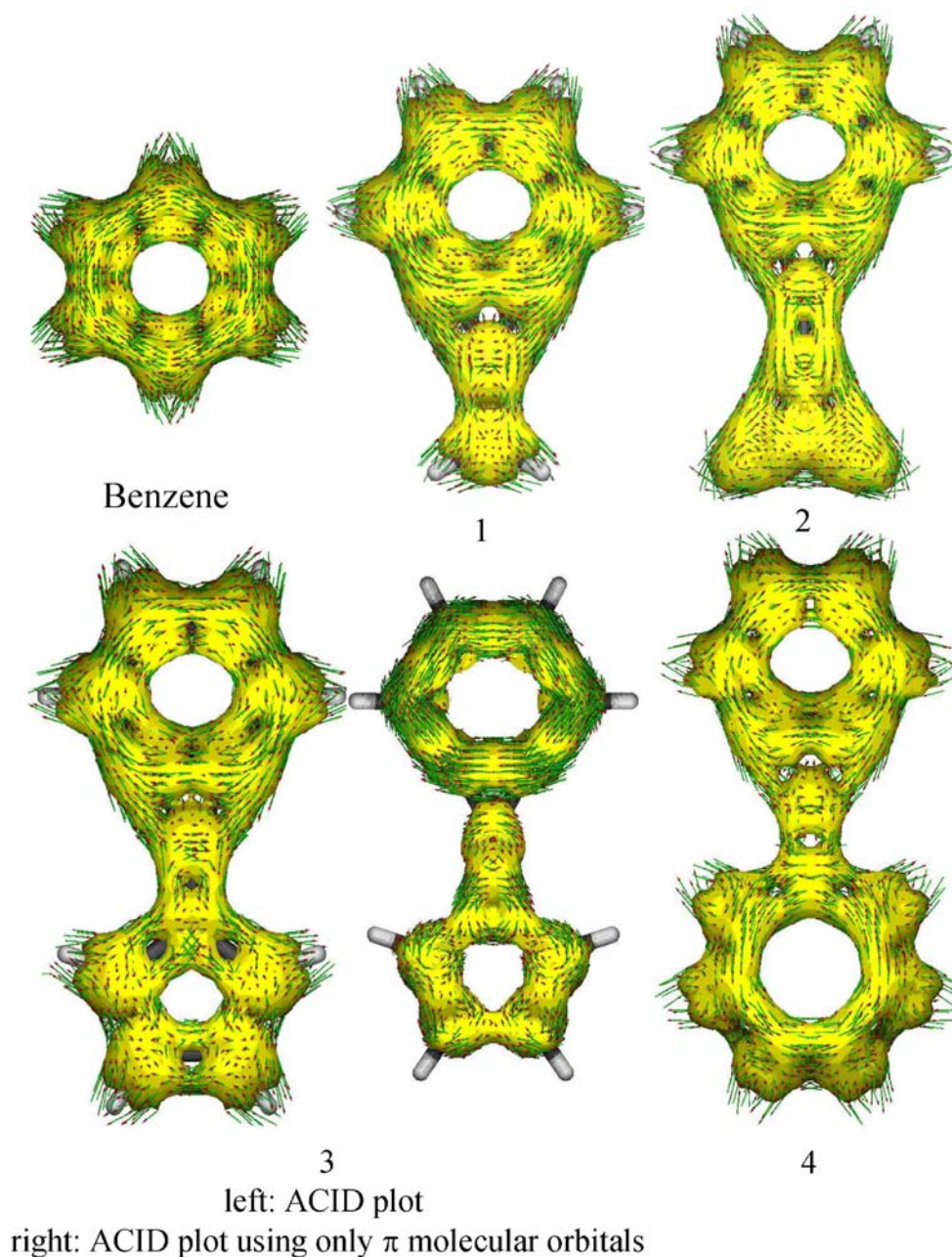


CPB, the cyclopentadiene presents a homogeneous slightly negative NICS. Cycloheptatriene has positive values of NICS along all the axis, decreasing its antiaromaticity as we move away from the molecule's plane.

Spatial NICS [14] is the result of project NICS's values calculated in different points of a three-dimensional grid on an electron density isosurface. We took an electron density isosurface equal to 0.05 (see Fig. 3). The benzene ring stands out from the rest of the molecule in each case, with a strong red colour. Looking at the lateral view, external hydrogens contained in the molecule's plane are blue (for example, in Fig. 3 the lateral view is shown for **2**), while the overlapping regions below and over the plane have

much more negative NICS values, since it is in that part that the delocalized ring current is stronger. The localization of the double bonds of cyclopropene and cyclopentadiene rings in **2** and **3** can also be easily observed. It is also meaningful that the cycle of three members of CPB, with high NICS(0) values, is not so important in this spatial view of NICS. The reason is, one more time, that those values are due to the σ contribution as we said above. Finally, the molecule **4**'s cycloheptatriene appears with a strong blue colour, showing its antiaromaticity character. It is important to note that what we see in Fig. 3 is just a representative isosurface selected to compare the molecules. The scale goes from -20 to 0 , but there are NICS values higher than

Fig. 4 ACID plots. An isosurface of electron density equal to 0.05 was selected



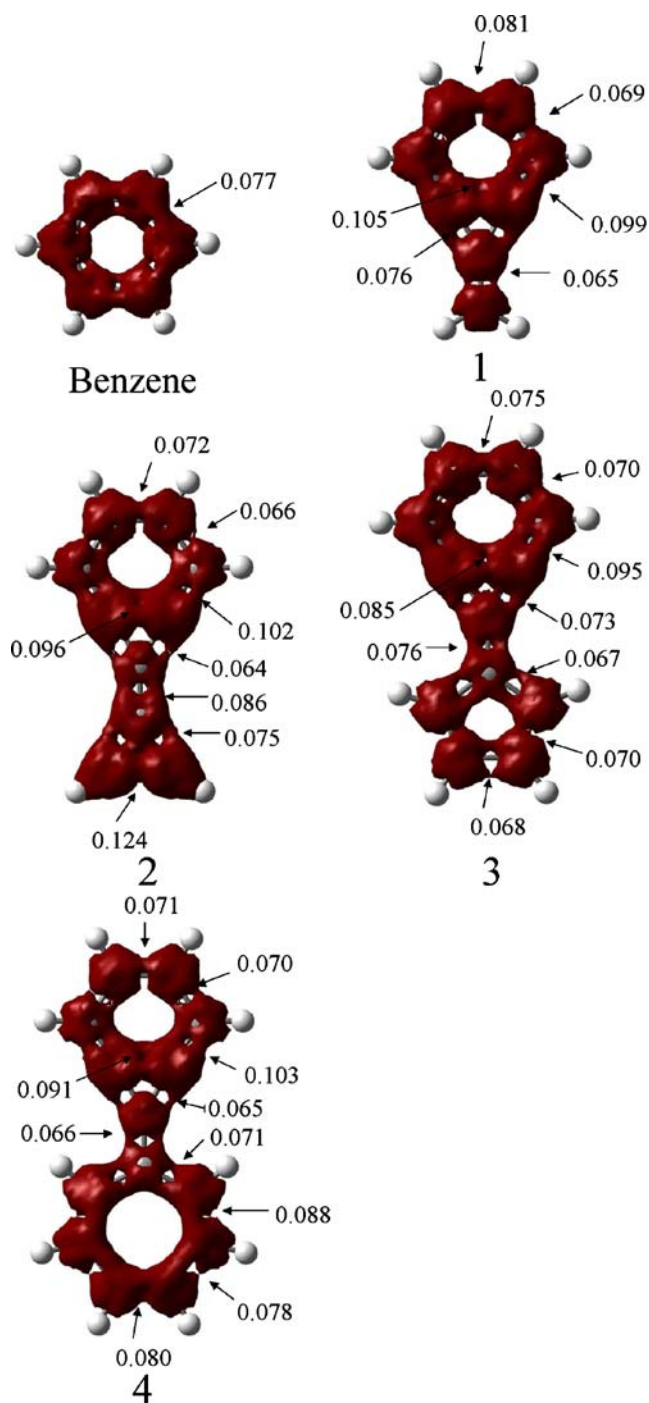


Fig. 5 Critical isosurface values. Anisotropy isosurface value is equal to 0.06

0, as we saw in NICS along the perpendicular axis. In fact, there is a significant set of points with $\text{NICS} = +5.0$ or higher in the cycloheptatriene of molecule **4**.

Anisotropy of the induced current density (ACID) ACID, the anisotropy of the induced current density, is a scalar field. ACID allows us to easily visualize the aromaticity in the molecule, showing the aromatic or antiaromatic character of the different rings. Figure 4 shows the

isosurfaces obtained for a 0.05 value; over them, density vectors were plotted. Therefore, we can analyze if there is or there is not continuity in the isosurfaces (that is, if electron delocalization takes place). In Fig. 4 we see the sense of turn of the induced ring current in the benzene molecule. The external magnetic field goes in the positive sense of the z axis, which is out of plane, pointing towards us. The turn is in agreement with the left hand rule, like clockwise: thus we have a diatropic current, typical of aromatic compounds. Inside the benzene molecule a small paratropic current can be observed, opposite to the first one, due to σ electrons. In molecule **1** the benzene ring is very similar. The same trend is observed in the cyclopropane ring, which shares the delocalized current with the neighbour ring. Therefore, the rings do not have their own current: the current belongs to the whole molecule. Molecule **2** is similar to the last one, with a delocalized current all over it. Cyclopentadiene ring of molecule **3** shows a slightly different behaviour. The vectors do not have a clear orientation. In this case, it is more useful to eliminate the σ contribution and check that the π current really is diatropic (see also Fig. 4, ACID plot using only π molecular orbitals). Finally, in molecule **4** there are clearly two different currents: one in the CPB fragment (diatropic) and one strong paratropic ring in the heptacyclopentatriene fragment.

The extent of the conjugation can be quantified by the critical isosurface value (CIV) at which the ACID boundary surface topology changes. This means that at CIV the delocalization current is interrupted. The smaller the CIV is, the weaker delocalization we have. Figure 5 shows the CIVs for molecules **1–4**. All the bonds in benzene are equivalent, so there is a unique value for this molecule: 0.077. This value can be used as reference for the benzene rings in **1–4**. For example, in **1**, the benzene ring has very different CIVs. The highest values correspond to those with the largest electronic delocalization; in other words, where the induced current is stronger. It is also interesting to analyze what happens in the double bond that joins CPB fragment with the third ring. **1** and **4** have to lowest values (near to 0.065) while **2** has a higher value, 0.086; this fact agrees with the current which is extended over whole molecule **2**. Note also that in **4** the CIVs in the cycloheptatriene ring are very large, reflecting the strong antiaromatic current present in that molecule.

Table 5 Obtained values for geometric indexes HOMA and Bird

	Bird index	HOMA
Benzene	100.0000	0.9835
1	89.0042	0.9449
2	84.0783	0.8941
3	90.2580	0.9504
4	87.6441	0.9257

HOMA and Bird geometric indexes The obtained results are in Table 5. These indexes are used only in the benzene ring, the only one we can use to compare **1–4**, according to the nature of those indexes. The bigger the index is, the larger aromaticity we have. According to this, the order of aromaticity predicted by these indexes is Benzene > **3** > **1** > **4** > **2**. It is important to note that both indexes predict the same relative aromaticity, so the agreement between them is very good. However, the correlation between these indexes and NICS(1) is more complex. The order predicted with NICS(1) is Benzene > **1** > **3** > **4** > **2** (Table 5). Only the position of **1** and **3** are changed but according to their geometric indexes both molecules have a fairly similar aromaticity. Moreover, taking into account that they are two measures of a very different nature, the correlation is acceptable.

Conclusions

The aromaticity of fulvene methylidencyclopropabenzene and three derivated fulvalenes was analyzed using different tools: magnetic susceptibility and anisotropy of magnetic susceptibility, NICS, ACID, and geometric indexes. All measures show that these compounds are strongly aromatic, globally even more so than benzene; furthermore, there are regions of very different aromaticity inside each molecule, as we observed with the local measures. That is, although the benzene ring in MCPB and in molecules **2**, **3** and **4** is less aromatic than in the benzene molecule, the molecule's other cycles make this fact possible. Looking at the global measures, the least aromatic compound is MCPB (**1**). Compounds with an additional carbocycle (with an odd number of atoms) show a higher aromaticity. This aromaticity increases from **2** to **3**, but it decreases for **4** due to the antiaromaticity character of the additional carbocycle.

As tools to quantify aromaticity, NICS and ACID were the most useful. NICS(0) and NICS(1) help us distinguish σ -aromaticity and π -aromaticity, showing very clearly the difference between the molecule's plane and the *p*-orbitals overlap region. ACID plots confirm the NICS results, showing the nature and intensity of all currents in each molecule; all of them are aromatic except the one corresponding to the cycloheptatriene of **4**.

Acknowledgements The authors express their deep gratitude to Dr. Herges for the ACID program, to Sonia Montes Romanillos for her kind help, and to the Centro de Supercomputación de Galicia (CESGA) for the use of their computers.

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