An Insight into the Local Aromaticities of Polycyclic Aromatic Hydrocarbons and Fullerenes

Jordi Poater, Xavier Fradera, Miquel Duran, and Miquel Solà*[a]

Abstract: In this work we quantify the local aromaticity of six-membered rings in a series of planar and bowl-shaped polycyclic aromatic hydrocarbons (PAHs) and fullerenes. The evaluation of local aromaticity has been carried out through the use of structurally (HOMA) and magnetically (NICS) based measures, as well as by the use of a new electronically based indicator of aromaticity, the *para* delocalization index (PDI), which is defined as the average of all the Bader delocalization indices between *para*-related carbon atoms in six-membered rings. The series of PAHs selected includes $C_{10}H_8$, $C_{12}H_8$, $C_{14}H_8$, $C_{20}H_{10}$, $C_{26}H_{12}$, and $C_{30}H_{12}$, with benzene and C_{60} taken as references. The change in the local aromaticity of the six-membered rings on going from benzene to C_{60} is analyzed. Finally, we also compare the aromaticity of C_{60} with that of C_{70}, open [5,6]- and closed [6,6]-$C_{60}NH$ systems, and $C_{60}F_{18}$.

Keywords: aromaticity · atoms in molecules theory · fullerenes · *para*-delocalization index · polycyclic aromatic hydrocarbons

Introduction

Fullerenes represent a novel class of aromatic compounds[1] with a three-dimensional delocalized electronic structure. The question of whether fullerenes should be regarded as fully aromatic molecules or not has been controversial ever since their discovery (for a review see reference [2]). It is generally accepted that fullerenes have an ambiguous aromatic character,[2–6] with some properties that support the aromatic view of these systems and others that do not. Their magnetic and NMR properties, for instance, clearly demonstrate that extensive cyclic delocalization of π electrons takes place in fullerenes, as expected for aromatic molecules. There is also broad evidence that fullerenes experience substantial ring currents.[7–11] This, together with their rather considerable stability, seems to stress their aromatic character.[5] However, evidence from chemical reactivity weighs against the aromaticity of these systems, since fullerenes are very reactive molecules that easily undergo a large variety of chemical transformations.[12–17] Not only do fullerenes behave in many reactions like poorly conjugated and electron-deficient alkenes,[18–20] but they also react mainly through addition reactions to the conjugated π system, which are basically driven by the reduction of strain.[4] Moreover, the enthalpy of formation of fullerenes[21] does not support an aromatic character either.[22] In addition, the existence of two types of bonds in C_{60} ([6,6]- and [5,6]-bonds)[23, 24] and eight different types of bonds in C_{70}[25, 26] indicates that a partial localization of the π-orbitals takes place in fullerenes. Finally, it is worth noting the existence of a $2(N+1)^2$ rule[27, 28] for spherical fullerenes equivalent to the $4N+2$ Hückel rule for planar PAHs. According to this rule, charged C_{60} systems with completely filled shells, such as C_{60}^{10+}, are much more aromatic than C_{60} and exhibit less pronounced bond length alternation.

Buckybowls are bowl-shaped polycyclic aromatic hydrocarbons (PAHs) made up of five- and six-membered rings arranged as in fullerene structures.[29–30] It is generally accepted that buckybowls display fullerene-like physicochemical properties, and in particular it has been shown that PAHs exhibit ring currents comparable to those in fullerenes.[33] Therefore, it can be assumed that the aromaticity of buckybowls is similar to that of fullerenes.

Several works have addressed the problem of aromaticity in fullerenes and in planar and curved PAHs. The experimentally determined and calculated homodesmotic stabilization energies of naphthalene, acenaphthylene, and pyracyclene indicate that naphthalene and acenaphthylene are clearly aromatic, while pyracyclene is marginally aromatic or antiaromatic.[34] The aromaticity in coronenes,[33] heterocoronenes,[35] corannulene,[33] and $C_{30}H_{12}$[36] has been analyzed by use of NICS and ^{13}C and ^{1}H NMR chemical shieldings. For these systems it has been found that five-membered rings have nonaromatic or slightly antiaromatic character, while six-membered rings display meaningful local aromaticities

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with some exceptions.[36–38] In general, six-membered rings vicinal to a five-membered ring are less aromatic than those not directly connected to a five-membered ring.[38] The local aromatic character of C_{60} and C_{70} has previously been studied by use of HOMA[6] and NICS[37] indices. The fact that C_{60} is found to be slightly less aromatic than C_{70} is attributable to the smaller proportion of five-membered rings in C_{70} than in C_{60}.[2, 3, 6] Remarkably, reduction of fullerenes increases the local aromaticity of five-membered rings.[39, 40] Finally, the local aromaticities of higher fullerenes and nanotubes have recently been studied by Bühl[37] and by van Lier and co-workers,[41] respectively.

In a previous work involving a study of the Diels–Alder reactions between 1,3-butadiene and several buckybowls[42, 43] we discussed how the chemical reactivity of buckybowls converges to that of C_{60} with increases in their size and curvature. We found that $C_{26}H_{12}$ is the smallest PAH that exhibits a C_{60}-like chemistry as far as the Diels–Alder cycloadditions are concerned, and that $C_{30}H_{12}$ has a reactivity almost indistinguishable from that of C_{60}. In view of the importance of the fullerenes, as well as the relevant effects of curvature on their chemical reactivity,[4, 43, 44] it seemed worthwhile to carry out a systematic study of the possible convergence of local aromaticity values on going from planar PAHs to C_{60}. Furthermore, from the point of view of aromaticity, the curved buckybowls are very attractive systems since they exhibit a compromise between strain and conjugation.[29] In this work we want to address the question of aromaticity in fullerenes and buckybowls, our aim being twofold. First, we analyze the changes in local aromaticities on going from planar PAHs such as benzene, naphthalene, and pyracyclene to curved PAHs such as $C_{20}H_{10}$, $C_{26}H_{12}$, and $C_{30}H_{12}$, and on to C_{60}. Second, we compare the local aromaticities in C_{60} with those of C_{70} and of two interesting derivatives of C_{60}: $C_{60}NH$ and $C_{60}F_{18}$. The $C_{60}NH$ system[45, 46] represents a possible case of homoaromaticity[47] in fullerenes, while $C_{60}F_{18}$[48–50] is a flattened fullerene possessing a benzene-like six-membered ring whose aromaticity is worth analysis.

According to Schleyer and Jiao,[51] aromatic systems are conjugated cyclic π-electron compounds that exhibit cyclic electron delocalization leading to bond length equalization, abnormal chemical shifts and magnetic anisotropies, and energetic stabilization. By this definition, the evaluation of aromaticity is usually based on structural, magnetic, and energy-based indices.[1, 52] The different indices of aromaticity can be divided into those that can be applied to describe the local aromaticity of a particular ring of the polycyclic system and those that give a global description of the aromaticity of the whole molecule. A local index of aromaticity is perhaps more useful than a global index for the whole molecule if we want to study the aromaticity of large polycyclic aromatic hydrocarbons (PAHs),[53] fullerenes,[2] or nanotubes.[41]

Abstract in Catalan: *En aquest treball quantifiquem l'aromaticitat local d'anells de sis membres en una sèrie d'hidrocarburs policíclics aromàtics plans i corbats (PAH), i ful·lerens. L'avaluació de l'aromaticitat local s'ha dut a terme mitjançant mesures estructurals (HOMA) i magnètiques (NICS), i també amb un nou indicador electrònic d'aromaticitat, l'índex de deslocalització para (PDI), que es defineix com la mitjana de tots els índexos de deslocalització de Bader (DI) entre carbonis en posició para en anells de sis membres. La sèrie de PAHs escollida inclou $C_{10}H_8$, $C_{12}H_8$, $C_{14}H_8$, $C_{20}H_{10}$, $C_{26}H_{12}$, i $C_{30}H_{12}$, amb el benzè i el C_{60} emprats com a referències. S'analitza l'evolució de l'aromaticitat local dels anells de sis membres quan anem del benzè al C_{60}. Finalment, també comparem l'aromaticitat del C_{60} amb la del C_{70}, els sistemes obert [5,6]- i tancat [6,6]-$C_{60}NH$, i el $C_{60}F_{18}$.*

Principal component analysis has revealed that aromatic compounds cannot in general be characterized by a single property, the multidimensional character of aromaticity being one of the basic features of this concept.[52, 54–56] As a result, it is recommendable to use more than one aromaticity parameter for comparisons restricted to some regions or groups of relatively similar compounds.[55] Thus, fully aromatic systems are those cyclic π-electron species that follow all the main aromatic criteria, while those that do not follow all of them should be regarded as partly aromatic.[54, 55] Herein, to deal with the multidimensional character of aromaticity, we have considered three probes of local aromaticity: namely, structure, magnetic properties, and electron delocalization.

As a structure-based measure, we have made use of the harmonic oscillator model of aromaticity (HOMA) index, defined by Kruszewski and Krygowski as given in Equation (1).[57, 58]

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum_{i=1}^{n}(R_{opt} - R_i)^2 \qquad (1)$$

Here n is the number of bonds considered, and α is an empirical constant fixed to give HOMA = 0 for a model nonaromatic system and HOMA = 1 for a system with all bonds equal to an optimal value R_{opt}, assumed to be achieved for fully aromatic systems. R_i stands for a running bond length. This index has been found to be one of the most effective structural indicators of aromaticity.[54, 59]

Magnetic indices of aromaticity are based on the π-electron ring current induced when the system is exposed to external magnetic fields. In this work we have used the nucleus-independent chemical shift (NICS), proposed by Schleyer and co-workers,[51, 60] as a magnetic index of aromaticity. This is one of the most widely employed indicators of aromaticity, and is defined as the negative value of the absolute shielding computed at a ring center or at some other point of interest in the system. Rings with large negative NICS values are regarded as aromatic. The more negative the NICS values, the more aromatic are the rings.

The degree of π delocalization in an aromatic compound is generally considered to provide a measure of its aromaticity. Indeed, several measures of delocalization derived from natural bond orbital analysis of the first-order density have been used to quantify aromaticity in five-membered heteroaromatic compounds.[61, 62] Also noticeable is the work carried out by Moyano and Paniagua,[63, 64] who used local resonance energies obtained from Hückel localized molecular π orbitals to evaluate local aromaticities. Interestingly, Sakai[65, 66] has recently shown that the resonance energy increases when the gap between the weights of the CI coefficients of singlet coupling and polarization terms decreases, and has consequently proposed the use of this gap to evaluate aromaticity in six-membered rings. As an aromaticity criterion based on electron delocalization, the delocalization index (DI), $\delta(\mathrm{A,B})$,[67, 68] derived from Bader's Atoms in Molecules (AIM) theory[69–71] has recently been used.[72, 73] The $\delta(\mathrm{A,B})$ value is obtained by double integration of the exchange-correlation density over the basins of atoms A and B, which are defined from the condition of zero-flux gradient in $\rho(r)$ [Eq. (2)].[69–71]

$$\begin{aligned}\delta(\mathrm{A,B}) &= -\int_{\mathrm{A}}\int_{\mathrm{B}} \Gamma_{XC}(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2 - \int_{\mathrm{B}}\int_{\mathrm{A}} \Gamma_{XC}(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2 \\ &= -2\int_{\mathrm{A}}\int_{\mathrm{B}} \Gamma_{XC}(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2\end{aligned} \tag{2}$$

δ provides a quantitative idea of the number of electrons delocalized or shared between atoms A and B,[68, 74] so this index is clearly related to the idea of electron delocalization so often found in textbook definitions of aromaticity. We have shown[73] that there is a satisfactory correlation between NICS, HOMA, and magnetic susceptibilities with the average of all delocalization indices of *para*-related carbon atoms (*para* delocalization index; PDI) in a given six-membered ring for a series of planar PAHs. In general, larger PDI indices go with larger absolute values of NICS and larger HOMA values, thus reflecting greater aromaticity.

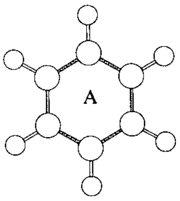
As mentioned above, six-membered rings in PAHs, fullerenes, and nanotubes display significant local aromaticities, while five-membered rings have nonaromatic or antiaromatic character. For this reason, our study is primarily focused on the local aromaticities of six-membered rings, for which HOMA, NICS, and PDI indices are used as aromaticity criteria. The local aromaticity of five-membered rings is only briefly commented on, by use of the HOMA and NICS indices. Evidently, the PDI index cannot be used to quantify the aromaticity in pentagonal rings, because five-membered rings do not have *para*-related carbon atoms.

Computational Methods

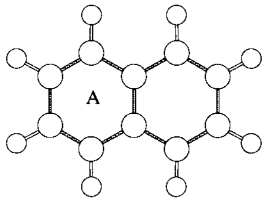
We used the AM1 semiempirical method[75] as implemented in Gaussian 98[76] to perform geometry optimizations with the restricted formalism. Calculations of NICS and PDIs were performed by the Hartree–Fock (HF) method with use of the 6-31G* basis set[77–79] at the AM1-optimized geometries (HF/6-31G*//AM1). The GIAO method[80] was used to perform calculations of NICS at the ring centers determined by the nonweighted mean of the heavy atom coordinates. Integrations of delocalization indices were performed by use of the AIMPAC collection of programs.[81] Pyramidalization angles were calculated by the π-orbital axis vector approach (POAV1)[4] as implemented in the POAV3 program.[82] In this method the local curvature of any carbon atom is defined by constructing a vector that forms equal angles to the three attached σ bonds, assuming that these bonds lie along the internuclear axes. For planar sp^2 centers this angle ($\theta_{\sigma\pi}$) is 90°, while for tetrahedral sp^3 carbons it is 109.47°. The pyramidalization angle is then defined as $\theta_{\sigma\pi} - 90°$. By this definition, the pyramidalization angle is 0° for sp^2 carbon atoms, 19.47° for sp^3 carbon atoms, and 11.64° for the carbon atoms in C_{60}.

Results and Discussion

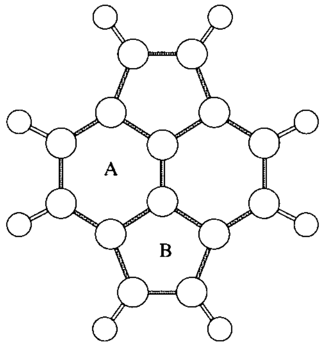
The local aromaticities in buckybowls; from benzene to C_{60}: In this section we analyze the changes in local aromaticities on going from planar PAHs such as benzene, naphthalene, and pyracyclene to curved PAHs such as $C_{20}H_{10}$, $C_{26}H_{12}$, and $C_{30}H_{12}$, and onward to C_{60}. $C_{30}H_{12}$ has been synthesized in



C_6H_6



$C_{10}H_8$



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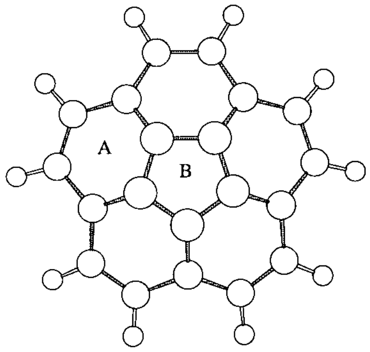

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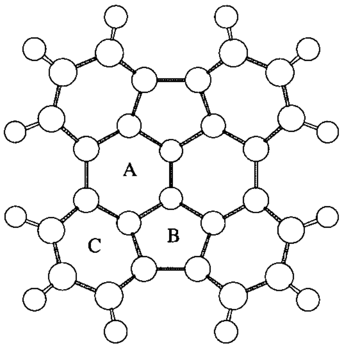

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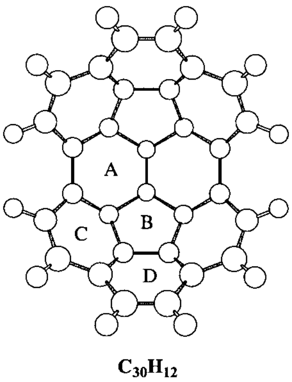
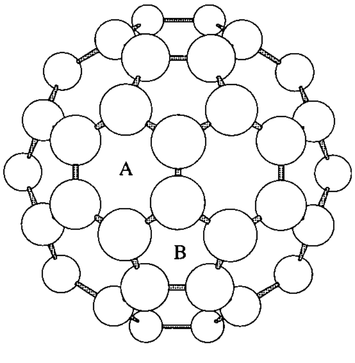


$C_{30}H_{12}$



C_{60}

three different isomeric bowl-shaped forms,[83–86] two of them with two pentagonal rings and the other one with three five-membered rings. In this work we have particularly considered only one of these three isomeric forms, corresponding to the buckybowl depicted.

As mentioned above, all aromaticity criteria were calculated at the HF/6-31G* level of theory by using the AM1 geometries. We used this semiempirical method instead of a more accurate ab initio method to compute the geometries for several reasons: first, the sizes of some of the systems studied prevented the use of ab initio molecular quantum-mechanical methods to perform optimizations, second, we have found by comparison with our previous results for C_6H_6, $C_{10}H_8$, and $C_{14}H_8$[73] that differences in HOMA, NICS, and PDI indices computed at the HF/6-31G* (HOMA and PDI) and HF/6-31+G* (NICS) levels by use either of the B3LYP/6-31G* or of the AM1 geometries are generally small, and third, the AM1 method yields reliable results for the geometries of C_{60},[87, 88] C_{70},[88] and also for the series of PAHs studied. For instance, Figure 1 displays a comparison between the experimentally determined and the B3LYP/6-31G* and AM1 geometries of corannulene. It is found that the AM1 bond lengths of corannulene are quite close to the experimentally determined values, the differences in bond lengths never being larger than 0.028 Å. Not only the bond lengths but also the curvature are well reproduced by the AM1 results, as one can see from the comparison between AM1 and experimentally determined pyramidalization angles for semibuckminsterfullerene, $C_{30}H_{12}$ (Figure 2). A good agreement between the experimentally determined and the AM1 pyramidalization angles is generally found, the largest difference being only 1.2 degrees.

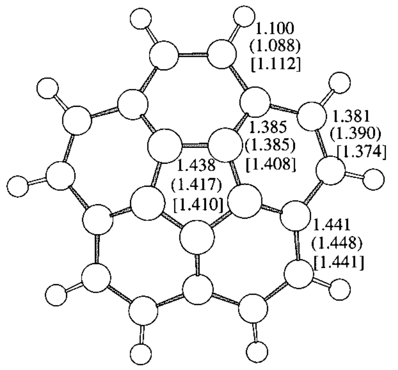


Figure 1. AM1 and B3LYP/6-31G* (in parentheses)[111] bond lengths (Å) of corannulene, $C_{20}H_{10}$. Single-crystal X-ray data[111] are presented in square brackets.

Table 1 lists the HF/6-31G*//AM1 values of the NICS, HOMA, and PDI indices, and the averages of the pyramidalization angles for several rings of the studied planar (C_6H_6, $C_{10}H_8$, and $C_{14}H_8$) and curved ($C_{20}H_{10}$, $C_{26}H_{12}$, and $C_{30}H_{12}$) PAHs, and also for C_{60}. It also lists the AM1 enthalpy barriers for the Diels–Alder cycloaddition between 1,3-butadiene and the central [6,6]-bond of each system,[42, 43] except for corannulene, for which there is no central [6,6]-bond.

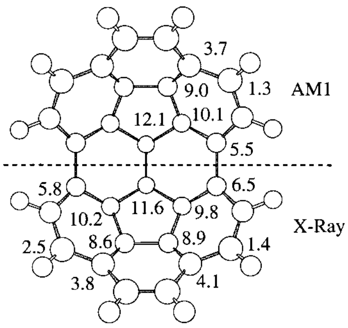


Figure 2. POAV pyramidalization angles calculated for the crystal structure[112] and for the AM1 optimized geometry of $C_{30}H_{12}$.

Table 1. HF/6-31G*//AM1 calculated values of NICS (ppm), HOMA, and *para*-delocalization (PDI) (electrons) indices, average pyramidalization angles for the carbon atoms present in a given ring (Pyr) (degrees), and AM1 enthalpy barriers (kcal mol^{-1}) for the addition of 1,3-butadiene to the central [6,6]-bond for a series of aromatic compounds.

Molecule	Ring	NICS	HOMA[a]	PDI	Pyr	$\Delta H^{\neq}$
C_6H_6	6A	−11.7	0.987	0.101	0.0	41.8[b]
$C_{10}H_8$	6A	−11.3	0.807	0.074	0.0	55.3[c]
$C_{14}H_8$	6A	−2.7	0.603	0.067	0.0	42.3
	5B	13.1	−0.205		0.0	
$C_{20}H_{10}$	6A	−8.6	0.652	0.058	4.6	
	5B	7.6	0.357		9.1	
$C_{26}H_{12}$	6A	−5.6	0.474	0.037	6.9	21.9[c]
	5B	3.9	−0.142		6.3	
	6C	−10.0	0.746	0.078	2.8	
$C_{30}H_{12}$	6A	−6.5	0.390	0.043	9.2	19.3[c]
	5B	6.8	0.113		10.1	
	6C	−9.4	0.652	0.061	5.1	
	6D	−8.1	0.614	0.057	4.6	
C_{60}	6A	−6.8	0.256	0.046	11.6	16.3[d]
	5B	6.3	−0.485		11.6	

[a] Equation (1) with $\alpha = 257.7$ and $R_{opt} = 1.388$ Å according to ref. [54]. [b] From ref. [87]. [c] From ref. [42]. [d] From ref. [88].

Let us first focus on the NICS, HOMA, and PDI values listed in Table 1. According to the NICS values, the order of local aromaticity of the six-membered rings is C_6H_6 > $C_{10}H_8$ > $C_{26}H_{12}$ (C) > $C_{30}H_{12}$ (C) > $C_{20}H_{10}$ > $C_{30}H_{12}$ (D) > C_{60} > $C_{30}H_{12}$ (A) > $C_{26}H_{12}$ (A) > $C_{14}H_8$. This order is well reproduced by the PDI values, except in the cases of $C_{26}H_{12}$ (C), which is found to be slightly more aromatic than $C_{10}H_8$, and $C_{14}H_8$, which is positioned after $C_{10}H_8$. HOMA indices also yield the same ordering for the hexagonal rings except in the cases of $C_{14}H_8$ (which according to HOMA is more aromatic than $C_{26}H_{12}$ (A)), $C_{26}H_{12}$ (A), which is found to be slightly more aromatic than $C_{30}H_{12}$ (A), and C_{60}, which is placed at the end. All methods agree in assigning clear aromatic character to the hexagonal rings of benzene, naphthalene, and $C_{20}H_{10}$, and to the outer six-membered rings of $C_{26}H_{12}$ (C) and $C_{30}H_{12}$ (C and D), while the inner six-membered rings of $C_{26}H_{12}$ (A), $C_{30}H_{12}$ (A), and C_{60} are found to be only moderately aromatic. The degrees of aromaticity of the six-membered rings in pyracyclene are more dependent on the method used to quantify aromaticity. Thus, according to the NICS value of close to zero, the six-membered ring of pyracyclene has a nonaromatic character, while both PDI and

HOMA indices favor a partial aromatic character for this ring. It is worth noting that Diogo et al.,[34] using thermochemical, structural, and NMR data, were also unable to reach a clear-cut answer regarding the aromatic or antiaromatic character of pyracyclene.

As pointed out earlier,[33, 36–38] the values in Table 1 show that the five-membered rings in PAHs and fullerenes have antiaromatic character while the six-membered rings display significant local aromaticities, with the possible exception of pyracyclene. Interestingly, six-membered rings connected to two five-membered rings—as in $C_{14}H_8$, $C_{26}H_{12}$ (A), $C_{30}H_{12}$ (A), and C_{60}—always have smaller local aromaticities than unconnected six-membered rings (C_6H_6 and $C_{10}H_8$) or six-membered rings connected to a unique five-membered ring ($C_{20}H_{10}$, $C_{26}H_{12}$ (C), and $C_{30}H_{12}$ (C and D)). The fact that the NICS values of the six-membered rings next to a pentagonal ring are slightly less negative than those without the five-membered rings has recently been mentioned in a study of aromaticity in cyclopenta-fused pyrene compounds.[38] The same study pointed out that the overall aromaticity of cyclopenta-fused compounds decreases with increasing number of externally fused five-membered rings. For $C_{26}H_{12}$ and $C_{30}H_{12}$, with different kinds of hexagonal rings, it is found that six-membered rings located in the rim, with bonded hydrogen atoms, are more aromatic than those in the hub.

Starting from the most aromatic and planar benzene, there is a convergence of the PDI values for the inner six-membered rings of the analyzed PAHs to the values of the six-membered rings of C_{60} in the sequence: $C_6H_6 > C_{10}H_8 > C_{14}H_8 > C_{20}H_{10} > C_{60} \approx C_{30}H_{12}(A) \approx C_{26}H_{12}(A)$.

The NICS values yield the same order, with the exception of $C_{14}H_8$, which is placed at the end. Finally, the order given by the HOMA indices—$C_6H_6 > C_{10}H_8 > C_{20}H_{10} > C_{14}H_8 > C_{26}H_{12}(A) > C_{30}H_{12}(A) > C_{60}$—also shows a similar trend from benzene to C_{60}. These results show that there is a certain convergence in the local aromaticity of the inner six-membered rings of PAHs when going from the most aromatic benzene to the partially aromatic six-membered rings of C_{60}.

Table 1 also lists the AM1-calculated enthalpy barriers to DA cycloadditions between 1,3-butadiene and those planar and bowl-shaped PAHs in this work that possess a central [6,6]-bond and show structural symmetry with respect to this [6,6]-bond being attacked. We have found that the local aromaticity increases when the curvature of the π-system decreases (compare, for instance, the values of A and C rings of $C_{26}H_{12}$) with some exceptions (compare the values of $C_{26}H_{12}(A)$ with those of $C_{60}(A)$). The carbon atoms of the central rings exhibit the largest pyramidalization angles, and the curvature then gradually decreases towards the rim. We found as a general trend that the most pyramidalized six-membered rings are those that have a lower local aromaticity, the most relevant exception being the six-membered ring in pyracyclene, which is only partially aromatic despite the planarity of the molecule. In spite of the existence of a certain relationship between local pyramidalization and aromaticity, the $\Delta H^{\neq}$ values of Table 1 seem to be related more to the pyramidalization angles than to the local aromaticity of the six-membered rings connected by the attacked [6,6]-bond. Thus, the six-membered rings of C_{60} are more aromatic than rings A of $C_{30}H_{12}$ or $C_{26}H_{12}$, according to NICS and PDI indices, and at the same time the [6,6]-bond in C_{60} is more reactive than the central [6,6]-bond in the ring fusion of two rings A of $C_{30}H_{12}$ or $C_{26}H_{12}$.

Finally, better to describe the aromaticity from a geometrical point of view, we separated the aromaticity index HOMA into energetic and geometric contributions, as proposed by Krygowski and Cyrañski.[54, 89] These workers have shown that the decrease in the aromatic character may be due either to an increase in bond length alternation (geometric term: GEO) or to the lengthening of the mean bond lengths of the ring (energetic term: EN). Both GEO and EN parameters, together with previously commented on HOMA values for the series in question, are listed in Table 2. From these values it is seen that in six-membered rings the decrease in aromaticity is due mainly to an increase in bond length alternation (GEO). In five-membered rings, on the other hand, the strong decrease in aromaticity is almost solely due to the bond elongation term (EN). Moreover, it is seen that EN and GEO terms are uncorrelated. Similar observations have already been reported by Krygowski and Cyrañski.[54, 89]

Table 2. Separation of the aromaticity index HOMA into energetic (EN) and geometric contributions (GEO) for a series of aromatic compounds.

Molecule	Ring	HOMA[a,b]	EN[c]	GEO[d]
C_6H_6	6A	0.987	0.013	0.000
$C_{10}H_8$	6A	0.807	0.067	0.126
$C_{14}H_8$	6A	0.603	0.051	0.346
	5B	– 0.205	0.771	0.434
$C_{20}H_{10}$	6A	0.652	0.141	0.206
	5B	0.357	0.643	0.000
$C_{26}H_{12}$	6A	0.474	0.174	0.352
	5B	– 0.142	0.999	0.143
	6C	0.746	0.117	0.136
$C_{30}H_{12}$	6A	0.390	0.253	0.358
	5B	0.113	0.883	0.004
	6C	0.652	0.170	0.178
	6D	0.614	0.156	0.230
C_{60}	6A	0.256	0.340	0.404
	5B	– 0.485	1.485	0.000

[a] Equation (1) with $\alpha = 257.7$ and $R_{\mathrm{opt}} = 1.388$ Å according to reference [54]. [b] HOMA = 1 – EN – GEO. [c] $\mathrm{EN} = f\alpha(R_{opt} - R_{av})^2$; $R_{av} = \frac{1}{n}\Sigma R_i$, with $f = 1$ as $R_{av} > R_{opt}$. [d] $\mathrm{GEO} = \frac{\alpha}{n}\Sigma(R_{av} - R_i)^2$.

As a whole, we have shown in this section that the three local indices of aromaticity give almost the same order for the different rings of the PAHs studied. Noticeably, all aromaticity criteria coincide to indicate that benzene has the largest aromaticity among all the systems studied. All methods also show that, for the less aromatic inner six-membered rings, there is a convergence in local aromaticity on going from benzene to buckminsterfullerene. Finally, the results show that for bowl-shaped PAHs in general, the less pyramidalized rings possess the largest local aromaticities.

The local aromaticities in C_{70}, $C_{60}NH$, and $C_{60}F_{18}$: In this section we discuss the local aromaticities in C_{70} and in $C_{60}NH$ and $C_{60}F_{18}$, two interesting derivatives of C_{60} from the point of view of aromaticity. The local aromaticities of these compounds are compared to those of C_{60}.

C_{70} has a centrosymmetric, rugby ball shaped D_{5h} structure that can be imagined as arising from insertion of an equatorial belt of five six-membered rings between two eclipsed hemispherical fragments of C_{60}. Loss of symmetry on going from I_h symmetry in C_{60} to D_{5h} symmetry in C_{70} increases the number of different carbon atoms in the fullerene (from one to five), the number of chemically different C–C bonds (from two to eight), and the number of different rings (from two to five). The molecular structure of C_{70} is shown in Figure 3, together with the labels given to each ring and to each different bond according to the widely accepted nomenclature employed by Taylor and co-workers[90] for naming the five different carbon atoms and the eight distinct C–C bonds in C_{70}. As would be expected, the different bonds and rings display different reactivities[88, 91–95] and local aromaticities. The fact that the most reactive bonds are the a–b and c–c [6,6]-bonds, located in the region of the pole of C_{70},[88, 91–95] suggests that the most unreactive six-membered rings, situated in the equatorial belt, are more aromatic than those in the pole. To confirm this hypothesis we calculated the NICS, HOMA, and PDI indices for C_{70} (Table 3). HOMA and NICS values for C_{60} and C_{70} have already been calculated by Krygowski and Ciesielski[6] and by Bühl,[37] respectively.

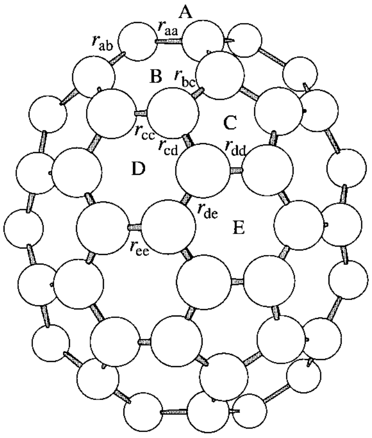


Figure 3. Structure of the C_{70} fullerene, together with the labels given to each ring, and to each bond studied.

The NICS, HOMA, and PDI values for the six-membered rings of C_{70} suggest that ring E has the largest aromaticity, followed by ring B, and lastly by ring D. In line with the results in the previous section, the most aromatic ring, ring E, also has the smallest average pyramidalization angle. However, ring B is found to be more aromatic than ring D despite the former being more pyramidalized. Unexpectedly, all aromaticity criteria indicate that ring B, located in the pole, is more aromatic than ring D, situated in the equatorial belt of C_{70}. With respect to the five-membered rings, as seen for the above series, both HOMA and NICS indicate that they are nonaromatic rings.

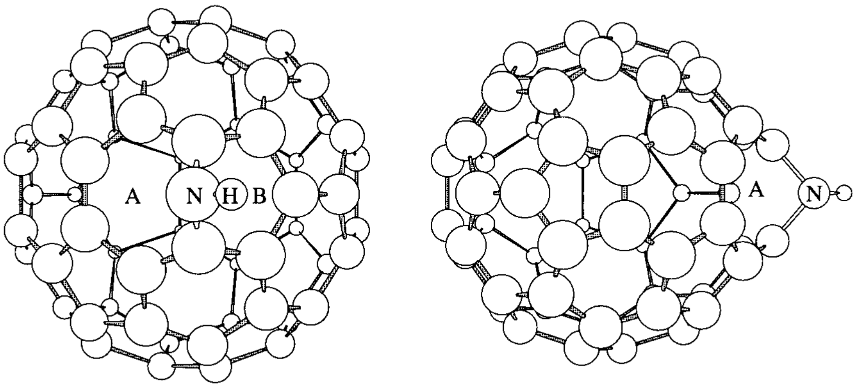
Table 3. HF/6–31G*//AM1-calculated values of NICS (ppm), HOMA, and *para*-delocalization (PDI) (electrons) indices and average pyramidalization angles for the carbon atoms present in a given ring (Pyr) [°] for C_{70} fullerene.

Molecule	Ring	NICS	HOMA[a]	PDI	Pyr
C_{70}	5A	2.8	–0.481		11.9
	6B	–11.5	0.294	0.046	11.8
	5C	–1.3	–0.301		11.0
	6D	–8.8	0.141	0.028	10.1
	6E	–17.3	0.697	0.059	9.6

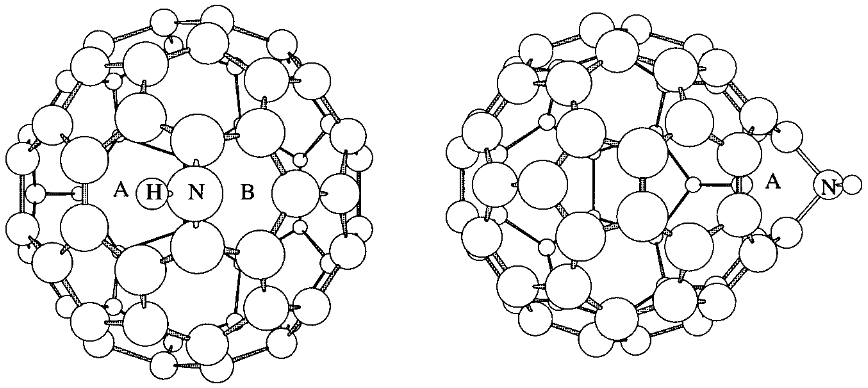
[a] Equation (1) with $\alpha = 257.7$ and $R_{opt} = 1.388$ Å according to reference [54].

Comparison of the results obtained for C_{70} with those found in the previous section for the PAHs studied and for C_{60} leads to some worthwhile conclusions. For instance, all aromaticity criteria agree in indicating that rings B and E in C_{70} are more aromatic than the six-membered rings in C_{60}. This is in agreement with the commonly accepted greater aromaticity of C_{70} than of C_{60},[2, 3, 6] despite the former being more reactive.[19, 88] The relative aromatic character of ring D of C_{70} depends on the method used to quantify aromaticity. NICS values give a greater aromaticity for ring D than for the six-membered rings of C_{60}, while, in contrast, HOMA and PDI indices indicate that ring D in C_{70} is less aromatic than the six-membered rings of C_{60}. In this case, as different indices of aromaticity provide different results, it is unsafe to draw definitive conclusions on the relative aromaticity of ring D of C_{70} as compared to the six-membered rings in C_{60}. Indeed, since the different available measures of aromaticity are based on diverse manifestations of this phenomenon, it is not surprising that distinct aromaticity indices may in some cases yield different results.[55] Somewhat surprising are the large values of the NICS index for rings E (–17.3 ppm) and B (–11.5 ppm), clearly superior even to that of benzene (–11.7 ppm) in the case of ring E. In contrast, the HOMA and PDI indices for the six-membered rings of C_{70} are always smaller than those of benzene and close to the values obtained for the six-membered rings of C_{60}. In particular, one may expect that ring B in C_{70}, which has almost the same geometric environment and average pyramidalization angle as the six-membered rings of C_{60}, should exhibit a similar aromaticity. Indeed, HOMA and PDI indices predict that both rings should possess comparable aromaticities. The NICS values, however, clearly assign greater aromaticity to ring B of C_{70}.

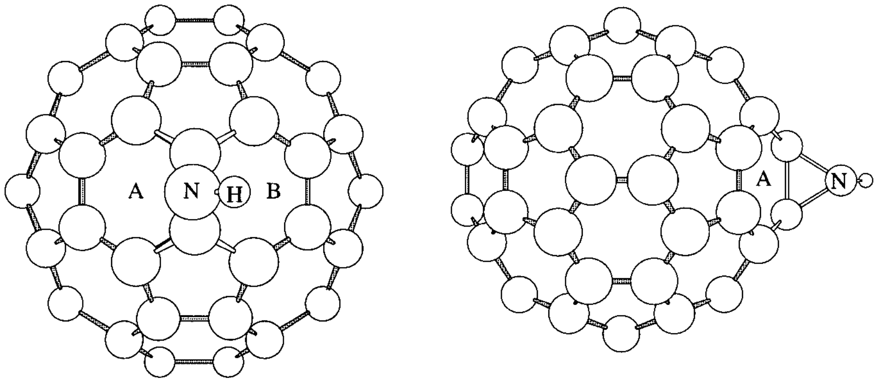
The next system that we studied was $C_{60}NH$. Imino[60]fullerenes such as $C_{60}NH$ can be obtained by two different synthetic routes. First, they can be generated through direct [1+2] cycloaddition between C_{60} and oxycarbonylnitrenes produced in situ either by thermal elimination of N_2 from organic azides or by base-catalyzed α-elimination of *O*-4-nitrophenylsulfonylhydroxamic acid derivatives.[96–99] Second, they can also be formed through 1,3-dipolar cycloaddition between organic azides and C_{60}, followed by thermal or photochemical N_2 extrusion.[94, 100–108] Direct oxycarbonylnitrene addition to C_{60} predominantly yields the closed [6,6]-aza-bridged adduct as the major regioisomer, together with certain amounts (ca. 10%) of open [5,6]-aza-bridged adducts (also termed homofullerenes or fulleroids). The outcome of the addition of organic azides to C_{60} depends on the nature of the azide substituent,[101] although under thermolytic conditions the open [5,6]-aza-bridged is usually the main adduct observed. So far, only the closed [6,6]- and open [5,6]-aza-bridged adducts have been found in these kind of reactions. The other two possible regioisomers, the so-called open [6,6] and closed [5,6], have never been observed. The origin of their instability is attributed to the fact that hypothetical open [6,6]- or closed [5,6]-structures require the introduction of three and two unfavorable double bonds, respectively, in five-membered rings.[109]



C_{60}NH-open-[5,6]/5



C_{60}NH-open-[5,6]/6



C_{60}NH-closed-[6,6]

Figure 4. Structures of the C_{60}NH fullerene isomers: open [5,6]/5, open [5,6]/6, and closed [6,6], together with the labels given to each different ring studied.

Our study focused on the two most stable isomers of C_{60}NH:[46] the open [5,6]- and the closed [6,6]-structures. Remarkably, in the case of the C_{60}NH open [5,6]-regioisomer, two possible structures exist: the so-called [5,6]/5- and the [5,6]/6-structures. The difference lies in the fact that while the hydrogen atom in the [5,6]/5-structure faces up the pentagonal ring, the hydrogen atom in the [5,6]/6-structure faces up the hexagonal ring. The structures of these isomers are shown in Figure 4, including the labels assigned to each ring studied, while Table 4 lists the NICS and PDI values for the six-membered rings analyzed in these three systems. In this case it was not possible to calculate the HOMA, because the non-planar shape of the rings that contain the NH group leads to meaningless results. Moreover, only two rings (A and B) were studied. For the open [5,6]-systems, ring B is the six-membered ring formed by the five carbons of the original five-membered ring in pristine C_{60} plus the nitrogen atom of the added NH group, while ring A is the six-membered ring containing the six carbon atoms of the original six-membered ring in C_{60}. By analyzing the aromaticity of these rings we aim to discuss the possible homoaromaticity in C_{60}NH species. The role of homoaromaticity is an important question in the electronic structure of fulleroids.[45]

The NICS and PDI values for these systems in Table 4 show that six-membered rings of closed [6,6]-C_{60}NH systems are partially aromatic, with NICS values of about −4 ppm and PDI values of approximately 0.03 electrons. Thus, in closed [6,6]-structures, the six-membered rings with the common [6,6]-bond to which the nitrene has been added partially preserve the original aromaticity, and our results therefore support the homoaromatic character of these compounds.[47] Rings A of open [5,6]-C_{60}NH systems are also partially aromatic, with NICS values ranging from −3 to −4 ppm and PDI values of approximately 0.03 electrons. This is in agreement with the belief that the π-electron system of C_{60} remains intact in fulleroids $C_{61}R_2$ and C_{60}NR.[20, 104] In this sense, open [5,6]-C_{60}NH systems can also be regarded as

Table 4. HF/6–31G*//AM1-calculated values of NICS (ppm) and *para*-delocalization (PDI) (electrons) indices, and AM1 relative enthalpies (kcal mol^{-1}) for a series of $C_{60}NH$ isomers.

Molecule	Isomer	Ring	NICS	PDI	ΔH[a]
$C_{60}NH$	open [5,6]/5	6A	−4.3	0.031	−5.1 (−0.7)
		6B	4.7	0.017	
	open [5,6]/6	6A	−3.0	0.029	−5.9 (−2.9)
		6B	5.3	0.016	
	closed [6,6]	6A	−3.6	0.026	0.0 (0.0)
		6B	−3.8	0.027	

[a] B3LYP/6–31G**//AM1 relative energies are given in parenthesis. From reference [46].

Table 5. HF/6–31G*//AM1-calculated values of NICS (ppm), HOMA, and *para*-delocalization (PDI) (electrons) indices, and average pyramidalization angles for the carbon atoms present in a given ring (Pyr) [°], for the flattened fullerene $C_{60}F_{18}$.

Molecule	Ring	NICS	HOMA[a]	PDI	Pyr
$C_{60}F_{18}$	6A	−14.3	0.922	0.085	1.3
	5B	−2.0	−7.154		11.1
	6C	−2.3	−7.275	0.009	12.8
	6D	−0.8	−6.697	0.009	14.5
	5E	−2.2	−5.515		11.8
	5F	2.5	−2.051		11.1
	6G	−12.1	0.473	0.053	9.5
	6H	−11.5	0.318	0.044	11.6
	5I	0.1	−0.341		12.1
	6J	−10.1	0.237	0.047	12.1

[a] Equation (1) with $\alpha = 257.7$ and $R_{opt} = 1.388$ Å according to reference [54].

homoaromatic species. Interestingly, ring A of open [5,6]/5-$C_{60}NH$, with the nitrogen electron pair facing up the hexagonal ring, is more aromatic than ring A of open [5,6]/6-$C_{60}NH$, despite the latter isomer being the more stable, and so the most stable open [5,6]/6 isomer does not have the most aromatic six-membered ring. This agrees with the results of Havenith and co-workers,[38] who found that the most stable representative of isomeric PAHs need not to be the most aromatic. Finally, it is worth noting that rings B in open [5,6]-$C_{60}NH$ species have anti- or nonaromatic character quite similar to that of five-membered rings in C_{60}.

The last system we deal with here is $C_{60}F_{18}$ fullerene,[48–50, 110] chosen for its flattened structure, which makes it interesting to compare to C_{60} in terms of aromaticity. The structure of this fullerene is reproduced in Figure 5 from two viewpoints to allow observation of the labels given to each different ring. The NICS, HOMA, PDI, and Pyr values for $C_{60}F_{18}$ are listed in Table 5.

NICS, HOMA, and PDI values for the six-membered rings in Table 5 clearly show that ring A, located at the flattened side of the fullerene, is the most aromatic ring in $C_{60}F_{18}$. Moreover, all three aromaticity criteria coincide in giving moderately aromatic character to rings G, H, and J, and nonaromatic character to rings C and D. In comparison with C_{60} values, rings G, H, and J—located on the nonplanar side of $C_{60}F_{18}$—are those most similar to the six-membered rings of C_{60} from an aromaticity point of view. They are also those rings with the geometric arrangement most similar to the six-membered rings in C_{60}. The average pyramidalization angles also follow the tendency given by the other three indices, the most aromatic ring (ring A) being almost planar (Pyr = 1.3°) and the less aromatic rings C and D being the most pyramidalized.

In line with the results obtained for C_{70}, $C_{60}F_{18}$ fullerene has quite large negative NICS values, with the aromatic A and G rings having larger NICS than benzene. Similarly, the HOMA and PDI values for all six-membered rings are smaller than those found for benzene. The most important result, however, is that application of all the aromaticity criteria to this fullerene orders the different rings with respect to aromaticity in the same way: A > G > H > J > C ≈ D, showing that the most planar six-membered ring is also the most aromatic and exhibits an aromaticity character similar to that of benzene.

Conclusion

In this work we have studied the change in the local aromaticity of six-membered rings on going from benzene to buckminsterfullerene through a series of planar and curved PAHs. The aromaticity of this series has been studied by means of the NICS, HOMA, and PDI indices of local

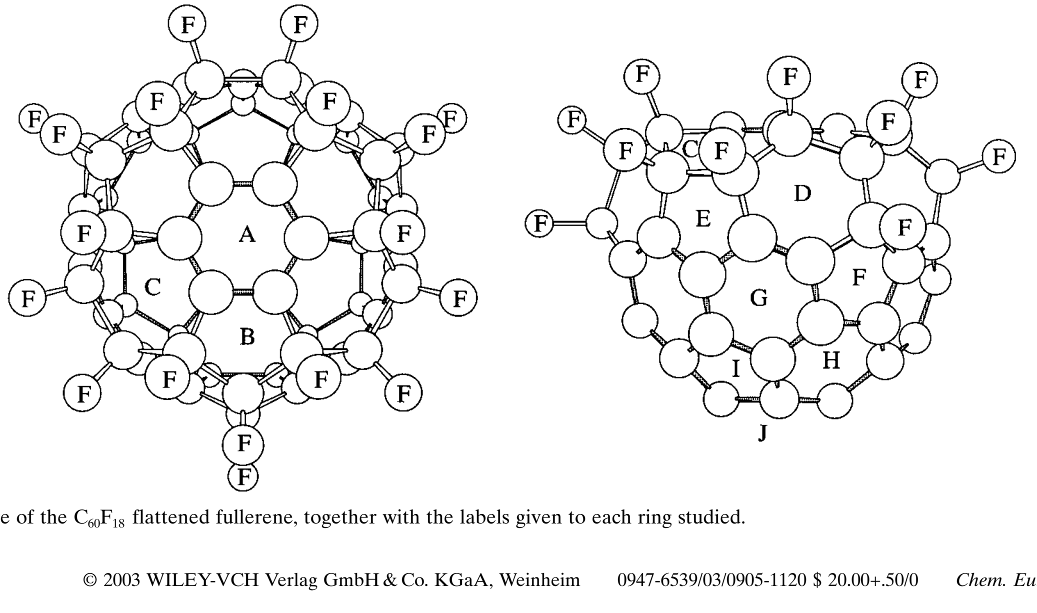


Figure 5. Structure of the $C_{60}F_{18}$ flattened fullerene, together with the labels given to each ring studied.

aromaticity, which take into account the magnetic, geometric, and π-electron delocalization properties, respectively, of the studied rings. We have shown that these local aromaticity criteria are useful tools for identifying regions of local aromaticity and antiaromaticity in PAHs and fullerenes. Except for a few cases, which can be attributed to the multidimensional character of aromaticity, all indices have provided the same qualitative results.

Six-membered rings appear usually to display notable local aromaticity, but there are also examples of small local aromaticities for inner six-membered rings connected to two five pentagonal rings. We have found that six-membered rings located in the rims of PAHs are more aromatic than those in the hub. For the less aromatic inner six-membered rings, there is a gradual reduction of aromaticity on going from benzene to C_{60}. In general, it has been found that the rings with the smallest average pyramidalization angles possess the largest local aromaticities. For C_{70}, we have also shown that two of its six-membered rings are more aromatic than the six-membered rings in C_{60} and that the six-membered ring located in the cap of C_{70} is not the least aromatic one. Finally, our results support the view of closed [6,6]- and open [5,6]-$C_{60}NH$ systems as homoaromatic species and show that the aromaticity of the more planar ring in $C_{60}F_{18}$ is quite close to that of benzene.

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