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Aromaticity of Fullerenes, the Way to their Functionalization (Review)

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Dedicated to Professor Mircea V. Diudea
In thanks for the opportunity to learn and cooperate

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ABSTRACT

Aromaticity is used to describe the durability and reactivity of structures containing delocalized π electrons. In this review article, the aromaticity of fullerenes patched with flowers of 6-and 8-membered rings, optimized at the HF and DFT levels of theory, is discussed in terms of HOMA and NICS criteria. The aromatic character of these nanostructures allows for functionalization and finally for increasing their solubility in polar solvents. The overall conclusion is that several of the yet hypothetical molecular nanostructures herein described are serious candidates to new medicinal products, as proposals for personalized medicine.

1 WHAT DOES MEAN AROMATICITY?

The phenomenon of aromaticity, as well as the synthesis and study of aromatic compounds and their properties, are of interest not only to chemists, but also to biologists, physicians and physicists. Annually there are several thousand articles in which one can find expressions like "aromatic" or "aromaticity" in the title, abstract or, finally, in key words [1]. Despite the widespread use of the term

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"aromaticity" or "aromatic", its ambiguity has not been ruled out and still raises a lot of controversies [2−6].

The definition of aromaticity is based on several criteria. The aromatic character is usually correlated with the stabilization energy of cyclic systems compared to their chain analogues, the shortening of bond length, the increase in their order in comparison to saturated analogues, as well as the existence of delocalized π-electron densities, susceptible to magnetic field influences. Aromatic compounds are more likely to undergo substitution reactions rather than addition. A compound is considered "aromatic" if all the criteria are met.

Aromaticity is used to describe the durability and reactivity of structures containing delocalized π electrons. The occurrence of only delocalization of π electrons does not justify the particular durability/stability that aromatic compounds have. Namely, the πelectron cloud must contain a certain number of electrons, fulfilling the Hückel rule. A cyclic (planar) π-electron system with (4n + 2) electrons is more stable than a system containing (4n) electrons. In addition to benzene and its higher analogues, such as: naphthalene, anthracene and phenanthrene, there are many heterocyclic compounds that are aromatic compounds [7]. Over 50% of organic compounds have an aromatic character, e.g., heterocyclic purine and pyrimidine rings of nucleotides and amino acids, included in nucleic acids and proteins. Also, fullerenes may have a partial aromatic character.

Aromaticity is a multidimensional concept [8−10]. The complexity of this phenomenon needs more than one parameter tobe described. A statistical surveys show that two or even three independent indices are necessary to describe the variability of the aromatic character [11], hence the diversity of indices "invented" for describing the aromaticity of compounds.

Four groups of criteria have been used to describe the aromaticity: (i) "energetic", indicating thermodynamic stabilization or destabilization (ii) "geometric", using changes in the bond length and angles associated with delocalization of electrons (iii) "electronic" which considers electron distribution and polarization and (iv) "magnetic" that shows the answer of such compounds to the magnetic field.

The most frequently used index of aromaticity based on a geometric criterion is the HOMA index (*Harmonic Oscillator Model of Aromaticity*). Originally defined on hydrocarbons [12], it was later extended to compounds containing hetero atoms [13]. The geometrical criterion says that, in aromatic compounds, the carbon-carbon bond lengths are the same and single and double bonds cannot be distinguished.

The energetic criterion is based on the resonance energy RE and aromatic stabilization energy ASE [5,14−18]. This concept originates in the Pauling's theory of valence bonds [19−22]. One of the effects of π-electron relocation is the increase in the thermodynamic durability of molecules compared to similar structures in which such relocation is not possible. The energy of resonance, which is the energy difference between the boundary structures and the actual molecule, is a measure of the durability of aromatic molecules. Pauling, Sherman and Kistiakowsky noticed that the structure of Kekulé and the actual structure of benzene differ in terms of energy [23−25]. Due to the fact that energy is related to the reactivity of a chemical compound and its physico-chemical properties, the energy criterion is often referred to as the basic condition of aromaticity. The energy of relocation can be determined from the heat of atomization or, generalizing, the heat of chemical reactions, using thermochemical data, determined both experimentally and calculated using quantum chemistry methods. Increasing the electron density in the ring of aromatic compounds makes these substances particularly easy to electrophilic substitution reaction, for example: nitration, alkylation, arylation, sulfonation, halogenation, in which the aromatic nature of the ring is preserved. Just as the addition reactions are typical for alkenes, substitution reactions are typical for the benzene ring. Benzene, as a resonant hybrid, maintaining a system of conjugated bonds, is therefore more likely to undergo substitution rather than addition reactions.

The reactivity criterion depends on the difference between the energy of the ground state of the system and the energy of the transition state, which makes it difficult to interpret the aromaticity of a chemical compound on the basis of this criterion. Because the relationship between changes in resonance energy and free enthalpy of activation depends on the type of reaction, various models of reactivity have limited application and can be used only for simple cases [26−27]. Schleyer proved that aromatic compounds are those exhibiting high magnetic susceptibility [28−29]. The basis of the research is the chemical shift of protons in the nuclear magnetic resonance spectrum [15,30]. The greatest influence on such chemical shifts have local diamagnetic currents, paramagnetic currents acting on further distances and annular electron currents [31]. An important factor using the influence of magnetic field on the electron rings is the magnetic exaltation susceptibility [32−33]. The values of this parameter depend on the ring size. For benzene, azulene, naphthalene and anthracene, it is 13.7, 29.2, 30.5 and 48.6, respectively [34]. Cyclic delocalization of π electrons results from equalizing the bond length and magnetic anisotropy [35−36]. In practice, the measurement of π-electron delocalization through the anisotropy of magnetic susceptibility is quite difficult. The NICS index ("nucleus-independent chemical shifts") is an effective magnetic criterion [29]. NICS is the negative value of atomic nuclei shielding [37] and is a popular tool used to assess aromaticity [Institute for Scientific Information, Philadelphia, 2004]. The use of NICS allows understanding of many issues related to systems containing electron delocalization [38]. These include cluster formation, transient states, metal complexing, homo-aromaticity, and spatiality (e.g., sphericity of the system) [39−50]. The method does not require any comparative structures or curve calibration. NICS for aromatic systems has negative values, while anti-aromatic compounds show positive values. However, NICS takes into account not only the level of π electron protection, but also the σ electrons, forming C-C and C-H bonds, free electron pairs and core electrons. The value of the NICS index depends on the size of the π system and substituent groups on the ring [51]. Therefore, for some chemical compounds, with a smaller or larger ring compared to the benzene ring, but the same number π electrons, the value of the NICS index can be overestimated or underestimated [52]. The NICS index estimates the local aromatic character by magnetic susceptibility of molecules, or more precisely, the electrons that, depending on the molecule, cover or unveil atomic nuclei. The original assumption was that the NICS value can be calculated in the geometric center of the chemical compound ring: in a(local) plane molecule, NICS is determined at a distance of 1Å over the center of the aromatic ring (NICS (1)) and under this ring (NICS (-1)). Like the chemical shift, NICS is expressed in ppm (parts per million). The NICS values for hydrocarbons such as benzene, naphthalene and anthracene range from -9 ppm to -10 ppm. The five-membered heterocyclic rings show higher NICS negative values: pyrrole (-15.1 ppm), thiophene (-13.6 ppm) and furan (-12.3 ppm). An example of an anti-aromatic compound, with a positive NICS value is cyclobutadiene (+27.6 ppm) [53].

NICS is not excluded by other methods, both magnetic, geometric or energetic. Statistical studies have shown that NICS correlates well with energy and the HOMA index (in case of 15 heterocyclic rings), and much less with other aromatic indices [Krygowski, Cyranski et al., 1999; Krygowski, Cyrański, 2000]. In case of porphyrin, the magnetic NICS index and the geometric HOMA index change monotonically [38]. Also, 18 independent rings in 9 hydrocarbons have a good linear correlation between the HOMA index and the NICS [54]. Krygowski et al. noticed a very good correlation between the aromatic indices HOMA and NICS and the energy calculated for a series of benzene ring containing hydrocarbons [38,54]. HOMA and NICS descriptors of aromaticity were used to describe the aromaticity, not only in biochemical compounds (such as nucleobases in DNA/RNA and amino acids in the protein environment) but also in inorganic compounds, such as fullerenes and other nanostructures.

2. NEW FULLERENES AND THEIR AROMATICITY

2.1. CIRCULENES

2.1.1 CIRCULENES WITH HEXAGONAL CORE

Circulenes are structures looking like a flower [55,56] with a core and surrounding petals (Figure 1) and with general formula [n:(p1,p2)*n*/2], where n is the size of the core polygon and p*i* are the polygonal petals [60].Three circulene-flowers: coronene, isocoronene and sumanene (Figure 2) were considered for the aromaticity test.

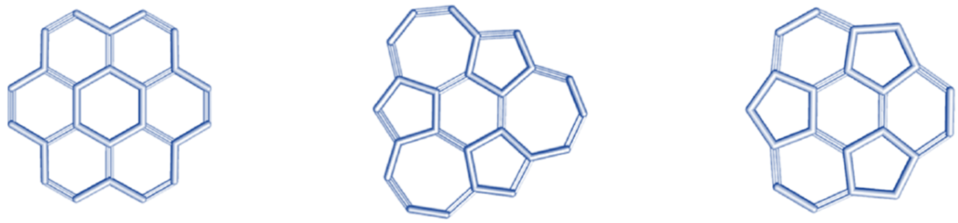
Figure 1. (**left**) Patches in fullerenes: joint patch in C140; (**right**) disjoint patch in C240.

Their aromaticity, mean stability and/or reactivity were discussed in terms of HOMA and NICS parameters, based on Hartree-Foch and DFT calculations. The local aromaticity of these circulenes was evaluated by NICS and HOMA indices [60](Table 1). Earlier, the molecules were optimized at B3LYP/6-31G(d) level by using G09 program[61].

Table 1. NICS and HOMA values of Circulenes after geometry optimization, at B3LYP/6-31G(d) level.

		NICS(0)	NICS(1)	HOMA
Coronene				
	R[6] core	−0.009	−4.429	0.618
	R[6] petal	−10.406	−12.453	0.764
Isocoronene				
	R[6] core	−2.908	−5.156	0.867
	R[7] petal	0.394	−2.712	0.013
	R[5] petal	−3.136	−5.637	−0.036
Sumanene				
	R[6] core	−2.767	−10.385	0.708
	R[6] petal	−10.080	−16.892	0.925
	R[5] petal	3.189	−5.192	−1.955

In case of coronene, the NICS values show aromatic character for the outer rings of the structure, while rings in the middle of the structures have lower aromatic or even non-aromatic character. The same observations are confirmed by the HOMA index [60]. The enhanced aromaticity of coronene results from the sextet migration current, like in case of naphthalene or anthracene [62].



coronene [6:66]_24 isocoronene [6:(5,7)3]_24 sumanene [6:(5,6)3]_21

Figure 2. Circulenes with hexagonal core.

Computations of the NICS(0) index for [6:(5,7)$_3$] isocoronene (Figure 2, middle) provide low negative values, indicating a low aromatic character [60] and close values for both the central 6-membered and the 5-membered rings of this polycyclic structure (Table 1). Contrarily, the 7-membered rings show positive values of NICS(0), what suggests a non-aromatic character. The NICS(1) index provides “more negative” values. On the other hand, the HOMA values show a different trend compared to both of the NICS indices, suggesting a more pronounced aromatic character of the central benzenic ring [63]. For sumanene (Figure 2, right), the values of the NICS(0) and NICS(1) indices show an anti-aromatic character of the pentagons and a strong aromatic character of the outer benzene rings (Table 1). Also, in this case, the HOMA data are close to NICS for consecutive, appropriate rings [60].

The coronene and sumanene fragments can be inserted into tetrahedrally spanned fullerene3D-structures (Figure 3).

Cor_T_84 Sum_T_84

Figure 3. The tetrahedrally spanned fullerenes patched by coronene and sumanene.

Table 2. Aromaticity (HOMA and NICS indices) of coroneneand sumanene patches in the tetrahedrally spanned fullerenes (Figure 3) (optimized at HF/6-31G(d,p); B3LYP/6-31(d,p) levels of theory) [60].

Structure	Substructure	NICS(−1)	NICS(0)	NICS(+1)	HOMA
Cor_T_84					
HF	$R_{6,core}$	−5.258	−0.789	−5.257	0.525
	$R_{6,plane}$	−16.429	−11.928	−11.342	0.908
	$R_{6,bound}$	−13.533	−4.518	−1.812	0.047
	patch				0.374
	Molecule				0.348
B3LYP	$R_{6,core}$	−9.184	−1.749	−2.808	0.529
	$R_{6,plane}$	−16.555	−12.123	−11.443	0.804
	R6,bound	−14.554	−5.532	−2.259	0.162
	patch				0.422
	Molecule				0.392
Sum_T_84					
HF	$R_{6,core}$	−11.775	−2.313	−2.078	0.849
	$R_{6,plane}$	−16.264	−11.349	−9.801	0.896
	R6,bound	−7.314	1.773	2.203	−1.685
	patch				−0.548
	Molecule				−0.476
B3LYP	$R_{6,core}$	−11.807	−2.437	−1.798	0.889
	$R_{6,plane}$	−16.177	−11.067	−9.047	0.850
	$R_{6,bound}$	−7.006	2.779	2.117	−1.162
	patch				−0.296
	Molecule				−0.229

Cor_T_84 and Sum_T_84 can be derived from the fullerene C_{84} and they can also be considered as tetrahedral junctions of nanotubes [64].

The values of total energy (**E_{tot}**), total Energy per number of C atoms in the structures (**E_{tot}/C**) and HOMO-LUMO gap **(HL Gap)** show a pertinent stability of these two tetrahedral structures. The highest aromaticity was found for the free hexagons $R_{6,\ plane}$, next for the $R_{6,\ Core}$ and finally the bound hexagons of Cor_T_84 molecule, estimated by both indices NICS(−1) and HOMA (Table 2). Here, the HOMA index was calculated for a patch and the whole molecule. The NICS values exhibit the highest aromaticity of the outer R_6 rings in comparison to the core hexagon in Sum_T_84 (Figure 3, right). The NICS(−1) values exhibit anti-aromatic character in the pentagons, while estimated values of NICS(+1) show still aromatic, but with lower values in comparison to the core hexagon. In case of HF-data, the HOMA values follow the trend of NICS(0) and NICS(−1) values while in the DFT-optimized structure the trend of HOMA values is different from that of NICS data.

2.1.2. CIRCULENES WITH OCTAGONAL CORE

The aromatic character of three circulenes with octagonal core (Figure 4) and petals consisting of 5-, 6 and 7-rings was also discussed [60].

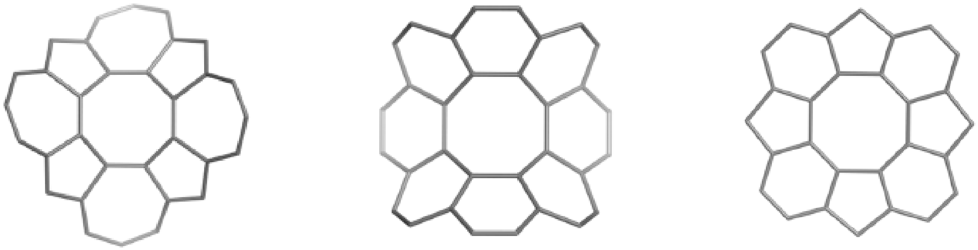

[8:(5,7)4]_32 [8:(6)8]_32 [8:(5,6)4]_28

Figure 4. Circulenes with octagonal core.

NICS(0) and HOMA values were calculated for the 8-membered central ring and the petal-rings of the studied circulenes with octagonal core; the values are listed in Table 3 [60].

Table 3. NICS(0) values for the 8-flowers in Figure 4 (optimized at the B3LYP/6-31G(d) level). Data for the petal rings in circulenes with hexagonal core [60] are shown for comparison (in round brackets).

	Structure	**Core**	**Petals (5 atoms)**	**Petals (6 atoms)**	**Petals (7 atoms)**
NICS (0)					
	[8:(5,6)4]	−2.330	−4.093 (−3.136)	-	1.842 (0.393)
	[8:68]	9.465	-	-7.788/−3.863 (−10.406)	-
	[8:(5,6)4]	8.172	0.686 (3.189)	-6.314 (−10.080)	-
HOMA					
	[8:(5,6)4]	−0.811	−0.983	-	−0.414
	[8:68]	−0.432	-	0.703/0.335	-
	[8:(5,6)4]	−0.524	−0.817	0.960	-

The largest aromatic character was found in 6-atom petals of circulenes [8:68] and [8:(5,6)4]. The 5-atom petals of circulenes [8:(5,6)4] show a two times lower aromatic character compared with 6-atom petals of circulenes [8:68]. As expected, the 7-atom petals in the flower [8:(5,7)4] show an anti-aromatic character. It means that for a saddle-shaped circulene, like the 8-coronene [8:68], the outer aromatic rings (even if they are all 6-rings) are no longer equivalent. After estimating the aromatic character based on index HOMA, it seems that the 6-atom petals of [8:(5,6)$_4$] flower have the most pronounced local aromatic character. A little smaller values of this index are shown by the 6-atom petals of [8:6$_8$]. For the 5- and 7-atom petals, the values of geometric index are negative, what corresponds to an anti-aromatic character.

Alternating values of local aromaticity indices, HOMA and NICS(0), show alternating properties of the 6-atom petals in the flower [8:68]. Also, circulene [8:(5,6)4], the only planar structure, has two equivalent C-atoms on each benzene unit with a uniform distribution around the molecule. In agreement with the fact that tetraoxa[8]circulenes represent real molecules [63], the most “aromatic” one is the 8-sumanene [8:(5,6)4].

Based on the results above, two different fullerenes, with 6-sumanene and 8-sumanene patches, were designed, Figures 5.

6-Sumanene C52([6:(5,6)3]4)

8-Sumanene C120 ([8:(5,6)3]6); [6:(5,6)3]8))

Figure 5. Fullerenes patched by: 6-sumanene (left) and 8-sumanene (right).

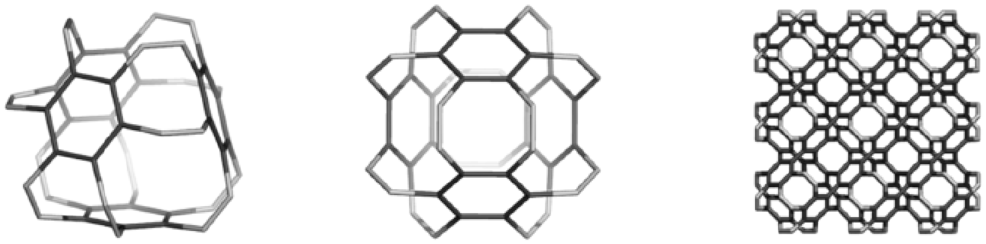
Table 4. NICS(0) and HOMA values for the fullerenes C52 and C120.

Structure/		**NICS(−1)**	**NICS(0)**	**NICS(+1)**	**HOMA**
C52					
	R[5] petal	−17.783	−2.292	−0.275	−0.093
	R[6] petal	−28.663	−15.704	−6.059	0.333
	R[6] core	−28.281	−11.372	−2.803	0.187
C120					
	R[5] petal	−12.058	−0.242	−0.711	−0.553
	R[6] petal	−16.646	−7.635	−3.589	0.537
	R[6] core	−16.746	−7.563	−3.565	0.821
	R[8] core	−3.498	5.164	6.196	−1.478

As expected, the values of NICS(−1) of the studied two structures 6-sumanene C52 and 8-sumanene C120, characterizing the inside cage electron density, show a more aromatic character in comparison to the outside cage described by NICS(+1). According to NICS(0) values, a more aromatic character of petals vs the core can be seen. In general, 6-sumanene C52 shows the same trend of aromaticity as 8-sumanene C120, and the HOMA values follow in general the trend of NICS values with one exception. Here, the 6-sumanene patch in C120, the 6-ring core was found more aromatic (0.821) than the 6-ring petal (0.537).

2.2. POLYBENZENES

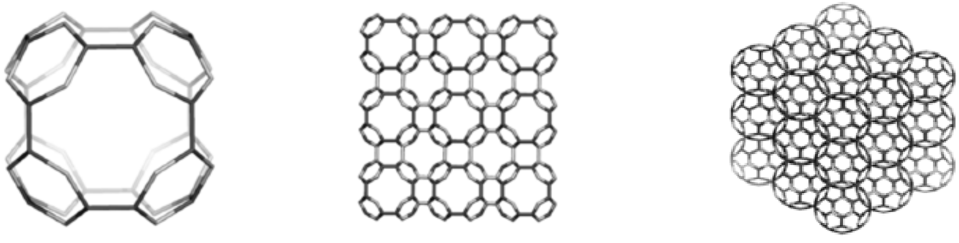
O'Keeffe et al. [65] proposed two 3D networks of benzene: the first one, is called 6.82 D (also polybenzene, Figure 6a, a-c) and belongs to the space group Pn-3m and has the topology of a diamond; the second structure (Figure 6a; d-f) is called 6.82 P and belongs to the space group Im-3m; the last one corresponds to the P-type surface. These networks represent embeddings [66] of the hexagon-patch in the two surfaces of negative curvature, D and P, respectively. These triple periodic minimal surfaces can embed networks of covalently bonded sp^2 atoms, called periodic Schwarzites [64, 67], in the honor of Schwarz [68, 69]. The two proposed structures show stability comparable, or even higher, to that of $C_{60}(I_h)$ [59, 70]. The structure 6.82 D was predicted to be an insulator while 6.82 P to be metallic. Zeolites [71] and spongy carbon [72, 73] represent Schwarzite structures. The networks were constructed [74] either by identifying or joining the common faces in the corresponding repeating units, BTA_48 and BCZ_48, respectively, Figures 6a. Face identification in case of the armchair-ended, tetrahedral unit BTA_48 is possible either by octagons R(8) or by dodecagons R(12). Identification by R(8) of the BTA_48 units, disposed at the center of the six faces of cube, leads to the 6.82 *fcc*-net (Figure 6a; c), with the topology of diamond; the corresponding R(8)-dimer we call the "*dia*-dimer" BTA2dia_88, Figure 6b; g. When R(12) are identified, the resulting oligomers are dendrimers (Figure 6b;k,l) and the R(12)-dimer is named "dendritic dimer" BTA2den_84 (Figure 6b; h). Dendrimers, after the second generation, completely superimpose over the BTA48_*fcc*-net (Figure 6b;i-l).



a
BTA_48 = 6.82 *D*

b
BTA_48 *fcc*-unit

c
BTA_*fcc*-net
(3×3×3)



d
BCZ_48 = 6.82 *P*

e
BCZ net (3×3×3)

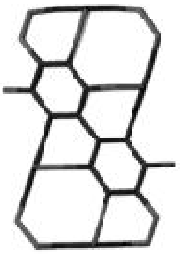
f
corner view

Figure 6a. Polybenzenes embedded in the *D*-surface.

All the proposed polybenzene structures are more aromatic (by HOMA values) than the reference fullerene C_{60} (table, Figure 6, middle). The BCZ_48 structure shows the highest value of HOMA. The other concerned structures are only a little less aromatic, cf this index. It seems that the C_C bond length is not the only parameter reflecting the π-electron conjugation, as limited by HOMA index. Probably, since C_{60} is all-carbon, the data cannot be directly compared to those of hydrogen-bearing molecules.

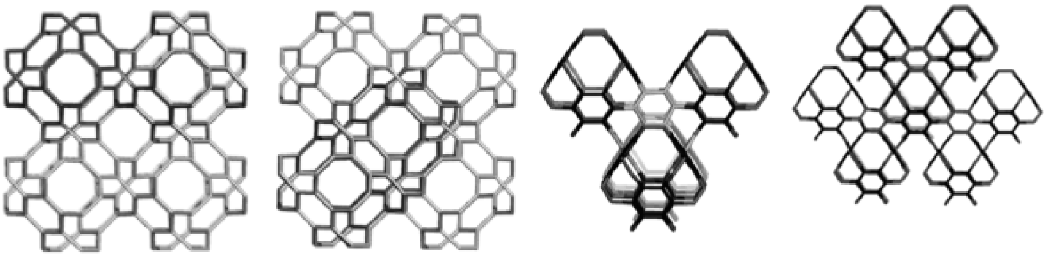
g
BTA_48 as R(8)-
BTA2dia_88

Polybenzene	HOMA R[6]
BTA_48	0.951
BCZ_48	0.989
BTA2dia_88	0.972
BTA2dend_84	0.975
BTA3dend_120	0.978
BTA4dend_156	0.978
BTA5dend_192	0.988
C60(Ih)	0.493



h

R(12)-BTA2den_84
dimer



i
R(8)-dimer in
BTA48-*fcc*-(2×2×2)

j
R(12)-dimer in
BTA48-*fcc*-(2×2×2)

k
BTA5dend_192

l
BTA17dend_624

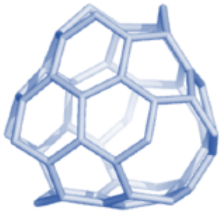
Figure 6b. Polybenzenes embedded in the D-surface and their HOMA index values (table, middle).

2.3. P-TYPE SURFACE COVERINGS

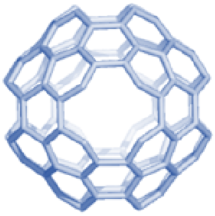
In experiments with fullerenes, it is possible that some cages appear spanned with the “open”-faces suitably joining to each other and eventually forming a nanotube. Such spanned fullerenes are called “*nanotube junctions*” [64]; based on their symmetry, tetrahedral, octahedral and icosahedral junctions can be distinguished. Due to similarity with the tetrahedral sp^3 hybridized carbon atom, the most interesting are the tetrahedral junctions; the valences are now nanotubes while the atom is an opened cage embedded in a surface of genus 2. An embedding is a representation of a graph on a surface S such that no edge-crossing occurs [66]. Genus is the number of handles needed to be attached to the sphere to make it homeomorphic to the surface on which a graph was embedded; also, it equals the number of connections of a given surface *S* [64, 67]. As the single C-atom, a tetrapodal junction can be used to build various nanostructures, such as diamondoids and multi-tori. Octahedral junctions (of genus g=3) appear in zeolites, of which associated graphs are embedded in the P-type surface. Icosahedral junctions are also possible, as they occur in icosahedral multi-tori [75]. Zeolites [71] are natural or synthetic alumino-silicates, with micro-porous structure, used as “molecular sieves”.

2.3.1. SUMANENE INCLUDING STRUCTURES

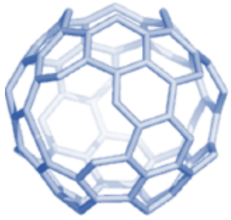
A Platonic tessellation is the covering by a single type polygon [64]. Four new structures were built [76−78] by using symmetry in embedding the triple hexagon patches (Figure 7, top row) or by applying map operations $Op_{2a}(S_2(M))$; M = tetrahedron T, or cube C (Figure 7, bottom row). The only C_3HexZ_104 structure is aromatic, based on HOMA, Figure 7.



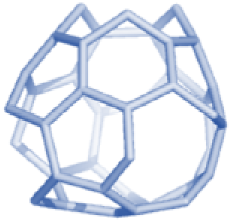
T_3HexZ_52; HOMA**(−0.131)**



C_3HexZ_104; HOMA**(0.258)**



T_3HextwZ_40; HOMA**(−0.583)**

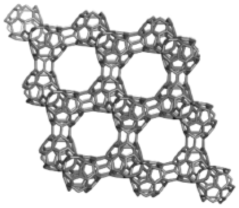


C_3HextwZ_80; HOMA**(−0.020)**

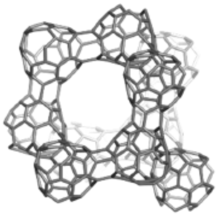
↓

The unit T_3HexZ_52 provides an “eclipsed” dimer, which can self-arrange to a hyper-pentagon; the join of 12 such hyper-faces forms a multi-torus 3HexZ20 of icosahedral symmetry .

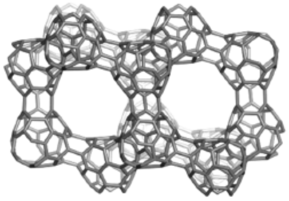
↓



Diamondoid network T_3HextwZ_(2,2,2)_1760



Ada_400



Dia_560

↓

The unit C_3HexZ_104, containing triple hexagon $3f6$ patches, forms a 3-periodic lattice, embedded in the P-surface.

P-type crystal network

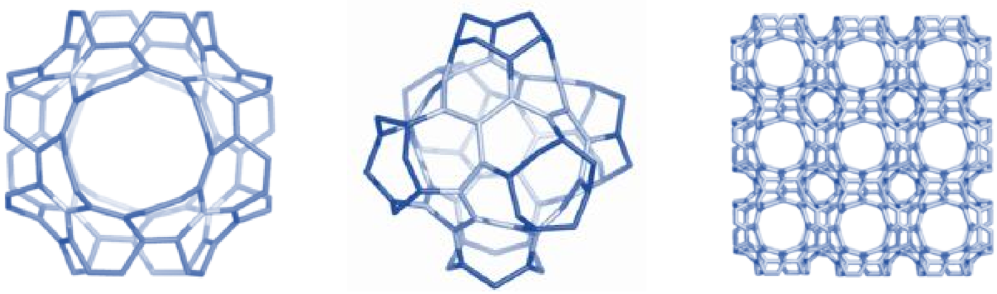
Figure 7. Triple hexagon-patched (H-ended) structures and HOMA value in brackets.

Anti-aromatic character is also shown by T_3HepA_52 and C_3HepA_104 (Table 6). These two structures belong to the triple-heptagon patched units.

Table 6. Triple heptagon-patched (H-ended) structures: HOMA index of aromaticity, after geometry optimization at HF/6-31G** and B3LYP/6-311+G**.

#	**Structure**	HF	**B3LYP**
1	C20	0.194	−0.361
2	T_3HepA_52	−0.951	−0.951
3	T_3HepA_104	−0.842	−0.244
4	C_{60}(Ih)	0.343	0.299

The units obtained by applying the septupling S_k, $k = 1, 2$ operations on the cube C, can form translatable crystal networks, as illustrated in Figure 8. This is the *kgn*-net, a 3-nodal network belonging to the group P432, related to the Klein graph [64]. The large hollows represent C_3HepA_104 (Figure 8, left, designed by $Op_{2a}(S_2(C))$ while the small hollows come from C_3HepZ_80 (Figure 8, middle, designed by $Op(S_1(C))$ [76].



C_3HepA_104
$v = 104$; $e = 132$; $f_7 = 24$; $g = 3$;
patch: 3 f_7

C_3HepZ_80
$v = 80$; $e = 108$; $f_7 = 24$; $g = 3$.

p-type crystal net
C_3HepA & C_3HepZ v=1944

Figure 8. Triple-heptagon patched units (left &middle) and the corresponding p-type network (right): the large hollows correspond to C_3HepA_104 (left) while the small ones to C_3HepZ_80 (middle).

5. CONCLUSIONS

The aromatic character is usually correlated with the energy stabilization of cyclic systems. Aromaticity is a multidimensional concept, needed to be described by more than one descriptor; among a variety of "aromaticity" indices, the actual review was focused only on HOMA (a geometric criterion index) and NICS (a magnetic criterion index).These indices were used to estimate the local aromatic character of the ring in several classes of nanostructures. Aromaticity of some hypothetical fullerenes, patched with flowers having the core of 6-and 8-membered rings, was discussed in terms of HOMA and NICS criteria. Polybenzenes and P-type surface structures covered by sumanene were also investigated.

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REFERENCES

1. ISI Web of Science, 2010
2. J. A. N. F. Gomes and R. B. Mallion, Aromaticity and ring currents, *Chem. Rev.* **101** (5) (2001) 1349−1383.
3. M. K. Cyrański, T. M. Krygowski, A. R. Katritzky and P. v. R. Schleyer, To what extent can aromaticity be defined uniquely?, *J. Org. Chem.* **67**(4) (2002) 1333−1338.
4. Z. Chen, C. S. Wannere, C. Crominboeuf, R. Puchta, R. v. P. Schleyer, Nucleus-independent chemical shifts (NICS) as an aromaticity criterion, *Chem. Rev.* **105**(10) (2005) 3842−3888.
5. M. K. Cyrański, Energetic aspects of cyclic pi-electron delocalization: Evaluation of the methods of estimating aromatic stabilization, *Chem. Rev.* **105** (2005) 3773−3811.
6. T. Heine, C. Corminboeuf and G. Seifert, The magnetic shielding function of molecules and pi-electron delocalization, *Chem. Rev.* **105**(10) (2005) 3889−3910.
7. T. M. Krygowski, M. K. Cyrański, G. Häfelinger and A. R. Katritzky, Aromaticity: a theoretical concept of immense practical importance, *Tetrahedron* **13**(56) (2000) 1783−1793.
8. A. R. Kartizky, B. Barczynski, G. Musumarra and D. Pisano, Aromaticity as a quantitative concept. 1. A statistical demonstration of the orthogonality of classical and magnetic aromaticity in five-and six-membered heterocycles, *J. Am. Chem. Soc.* **111**(1) (1989) 7−15.
9. K. Jug and A. Koester, Aromaticity as a multi-dimensional phenomenon, *J. Phys. Org. Chem.* **4**(3) (1991) 163−169.
10. M. K. Cyrański and T. M. Krygowski, Structural studies of disubstituted benzene derivatives 2 factor and regression-analyses of aromaticity of the

ring in para- disubstituted benzene-derivatives, *Pol. J. Chem.* **69** (7) (1995) 1088−1096.

11. T. M. Krygowski and M. Cyrański, Separation of the energetic and geometric contributions to the aromaticity. Part IV. A general model for the π-electron systems, *Tetrahedron* **52**(30) (1996) 10255−10264.
12. J. Kruszewski and T. M. Krygowski, Definition of aromaticity basing on the harmonic oscillator model, *Tetrahedron Lett.* **13**(36) (1972) 3839−3842.
13. T. M. Krygowski, Crystallographic studies of inter- and intramolecular interactions reflected in aromatic character of. pi-electron systems, *J. Chem. Inf. Comput. Sci.* **33**(1) (1993) 70−78.
14. L. Pauling and W. Whelang, The nature of the chemical bond. V. The quantum mechanical calculation of the resonance energy of benzene and naphthalene and the hydrocarbon free radicals, *J. Chem. Phys.* **1** (1933) 362−374.
15. V. I. Minkin, M. N. Glukhovtsev and B. Y. Simkin, *Aromaticity and Antiaromaticity:* Electronic and Structural Aspects, Wiley−Interscience, 1994.
16. P. v. R. Schleyer and H. Jiao, What is aromaticity?, *Pure Appl. Chem.* **68**(2) (1996) 209−218.
17. M. K. Cyrański, T. M. Krygowski, A. R. Katritzky and P. v. R. Schleyer, *J. Org. Chem.* **67**(4) (2002) 1333−1338.
18. M. K. Cyrański, P. v. R. Schleyer, T. M. Krygowski, H. Jao and G. Hohlneicher, Facts and artifacts about aromatic stability estimation, *Tetrahedron* **59**(10) (2003) 1657−1665.
19. L. Pauling and G. W. Wheland, The nature of the chemical bond. V. The quantum-mechanical calculation of the resonance energy of benzene and naphthalene and the hydrocarbon free radicals, *J. Chem. Phys.* **1**(6) (1933) 362−374.
20. R. Daudel, R. Lefebre and C. Moser, *Quantum Chemistry. Methods and Applications*, Interscience, New York, 1959.
21. L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry,* Cornell University Press, Ithaca, New York, 1960.
22. C. A. Coulson, *Valence*, 2nd ed., Oxford University Press, New York, 1961.
23. L. Pauling and J. Sherman, The nature of the chemical bond. VII. The calculation of resonance energy in conjugated systems, *J. Chem. Phys.* **1** (10) (1933): 679−686.

24. G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, Heats of organic reactions. IV. Hydrogenation of some dienes and of benzene, *J. Am. Chem. Soc.* **58**(1) (1936) 146−153.
25. A. Kekulé, Ueber einige Condensationsproducte des Aldehyds, *Liebigs Ann. Chem.* **168**(1872) 77−124.
26. P. v. R. Schleyer, M. Manoharan, H. Jiao and F. Stahl, Acenes: Is There a Relationship between Aromatic Stabilization and Reactivity?, *Org. Lett.* **3** (2001) 3643−3646.
27. J. Kruszewski and T. M. Krygowski, A quantum-chemical approach to the chemical definition of aromaticity, *Tetrahedron Lett* (1970) 319−324.
28. P. v. R. Schleyer, P. K. Freeman, H. Jiao and B. Goldfuss, Aromacity and antiaromacity in five-membered C_4H_4X rings systems: "Classical'' and "Magentic'' concepts may not be "Orthogonal'', *Angew. Chem., Int. Ed. Engl.* **34** (1995) 337−340.
29. A. Muñoz-Castro, Axis-dependent magnetic behavior of C_{60} and C_{60}^{10+}. consequences of spherical aromatic character, *Chem. Commun.* **51** (2015) 10287−10290.
30. G. Subramanian, P. v. R., Schleyer and H. Jiao, Haben die stabilsten anellierten Heterobicyclen auch den stärksten aromatischen Charakter?, *Angew. Chem.* **108** (22) (1996) 2824−2827.
31. P. Lazzeretti, Ring currents, *Prog. Nucl. Magn. Reson. Spectrosc.* **36** (2000) 1−88.
32. T. M. Krygowski and J. Kruszewski, Ilościowe kryteria aromatyczności Wydawnic two Politechniki Wrocławskiej, 1978.
33. H. J. Dauben, J. D. Wilson and J. L. Laity, Diamagnetic susceptibility exaltation as a criterion of aromaticity, *J. Am. Chem. Soc.* **90** (3) (1968) 811−813.
34. H. J. Dauben, J. D. Wilson and J. L. Laity, Diamagnetic susceptibility exaltation in hydrocarbons, *J. Am. Chem. Soc.* **91** (8) (1969) 1991−1998.
35. H. J. Dauben, J. D. Wilson and J. L. Laity, In: J. P. Snyder (ed.), Nonbenzoid Aromatics, vol 2, Academic Press: New York, pp. 167−206, Chapter 2, 1971.
36. R. C. Benson and W. H. Flygare, Molecular Zeeman effect of cyclopentadiene and isoprene and comparison of the magnetic susceptibility anisotropies, *J. Am. Chem. Soc.* **92** (26) (1970) 7523−7529.
37. W. H. Flygare and R. C. Benson, The molecular Zeeman effect in diamagnetic molecules and the determination of molecular magnetic

moments (g values), magnetic susceptibilities, and molecular quadrupole moments, *Mol. Phys.* **20** (2) (1971) 225−250.

38. M. K. Cyrański and T. M. Krygowski, Separation of the energetic and geometric contribution to aromaticity. Part X. The case of benzene rings in fused polycyclic benzenoid hydrocarbons, *Tetrahedron* **54** (49) (1998) 14919−14924.
39. G. Subramanian, P. v. R. Schleyer and H. Jiao, Are the most stable fused heterobicycles the most aromatic?, *Angew. Chem. Int. Ed. Engl.* **35**(22) (1996) 2638−2641.
40. H. Jiao, P. v. R Schleyer, Aromaticity of pericyclic reaction transition structures: magnetic evidence. *J. Phys. Org. Chem.* **11**(8-9) (1998) 655−662.
41. V. Gogonea, P. v. R Schleyer and P. R. Schreiner, Consequences of triplet aromaticity in 4nπ-electron annulenes: Calculation of magnetic Shieldings for open-shell species, *Angew. Chem. Int. Ed.* **37** (13−14) (1998) 1945−1948.
42. S. M. Ferrer and J. M. Molina, Theoretical calculations on $C_{30}H_{12}$ bowl-shaped hydrocarbons: NMR shielding constants, stability, and aromaticity, *J. Comput. Chem*. **20** (13) (1999) 1412−1421.
43. T. M. Krygowski and M. K. Cyrański, Two sources of the decrease of aromaticity: Bond length alternation and bond elongation. Part II. An analysis based on geometry of the singlet and triplet states of 4nπ annulenes: C_4H_4, $C_5H_5^+$, $C_6H_6^{2+}$, $C_7H_7^-$, C_8H_8, $C_9H_9^+$, *Tetrahedron* **55** (36) (1999) 11143−11148.
44. P. v. R. Schleyer, B. Kiran, D. V. Simon and T. S. Sorensen, Does $Cr(CO)_3$ complexation reduce the aromaticity of benzene?, *J. Am. Chem. Soc.* **122** (3) (2000) 510−513.
45. A. A. Fokin, B. Kiran, M. Bremer, X. Yang, H. Jiao, P. v. R. Schleyer and P. R. Schreiner, Which electron count rules are needed for four center three dimensional aromaticity?, *Chem. Eur. J.* **6** (9) (2000) 1615−1628.
46. R. B. King, Three-dimensional aromaticity in polyhedral boranes and related molecules, *Chem. Rev.* **101** (5) (2001) 1119−1152.
47. F. Stahl, P. v. R. Schleyer, H. Jiao, H. F. Schaefer, K. H. Chen and N. L. Allinger, Resurrection of neutral tris-homoaromaticity, *J. Org. Chem.* **67** (2002) 6599−6611.
48. C. Castro, C. M. Isborn, W. L. Karney, M. Mauksch and P. v. R. Schleyer, Aromaticity with a twist: Möbius [4 n] annulenes, *Org. Lett.* **4** (2002) 3431−3434.

49. Z. Chen, A. Hirsch, S. Nagase, W. Thiel and P. v. R. Schleyer, Spherical sila- and germa-homoaromaticity, *J. Am. Chem. Soc.* **125** (2003) 15507−15511.
50. Z. Chen, H. Jiao, D. Moran, A. Hirsch, W. Thiel and P. v. R. Schleyer, Aromatic stabilization in heterofullerenes $C_{48}X_{12}$ (X= N, P, B, Si), *J. Phys. Org. Chem.* **16** (2003) 726−730.
51. Z. Chen, C. S. Wannere, C. Crominboeuf, R. Puchta and R. v. P. Schleyer, Nucleus-independent chemical shifts (NICS) as an aromaticity criterion, *Chem. Rev.* **105** (2005) 3842−3888.
52. B. A. Hess Jr and L. J. Schaad, Hueckel molecular orbital. pi. resonance energies. New approach, *J. Am. Chem. Soc.* **93** (2) (1971) 305−310.
53. B. M. Smith and J. March, *Advanced Organic Chemistry*, Wiley, New York, 2001.
54. S. T. Howard and T. M. Krygowski, Benzenoid hydrocarbon aromaticity in terms of charge density descriptors, *Can. J. Chem.* **75** (1997) 1174−1181.
55. B. Szefler and M. V. Diudea, Quantum-mechanical calculations on molecular substructures involved in nanosystems, molecules, **19** (2014) 15468−15506.
56. M. Randić, Algebraic Kekulé formulas for benzenoid hydrocarbons, *J. Chem. Inf. Comput. Sci.* **44** (2004) 365–372.
57. A. Ciesielski, M. K. Cyrański, T. M. Krygowski, P. W. Fowler and M. Lillington, Super-delocalized valence isomer of coronene, *J. Org. Chem.* **71** (2006) 6840–6845.
58. A. Ciesielski, T. M. Krygowski, M. K. Cyrański and A. T. Balaban, Defining rules of aromaticity: A unified approach to the Hückel, Clar and Randić concepts, *Phys. Chem. Chem. Phys* **13** (2011) 3737–3747.
59. A. Löffler, N. Bajales, M. Cudaj, P. Weis, S. Lebedkin, A. Bihlmeier, D. P. Tew, W. Klopper, A. Böttcher and M. M. Kappes, Non-IPR C_{60} solids, *J. Chem. Phys.* **130** (2009) 164705.
60. R. Pop, M. Medeleanu, M. V. Diudea, B. Szefler and J. Cioslowski, Fullerenes patched by flowers, *Cent. Eur. J. Chem.* **11** (2013) 527–534.
61. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J.

Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

62. M. Randić, Aromaticity of polycyclic conjugated hydrocarbons, *Chem. Rev.* **103** (2003) 3449–3605.
63. M. V. Diudea, *Nanostructures-Novel Architecture*, M. V. Diudea (Ed.), Nova Publisher, New York, 2005, pp. 203–242.
64. M. V. Diudea and C. L. Nagy, *Periodic Nanostructures*, Springer, Dordrecht, The Netherlands, 2007.
65. M. O'Keeffe, G. B. Adams and O. F. Sankey, Predicted new low energy forms of carbon, *Phys. Rev. Lett* **68** (1992) 2325–2328.
66. F. Harary, *Graph Theory*, Addison-Wesley, Reading, MA, USA, 1969.
67. M. V. Diudea, *Nanomolecules and Nanostructures-Polynomials and Indices*, MCM Series 10, University of Kragujevac Press, Kragujevac, 2010.
68. H. A. Schwarz, *Über Minimalflächen* (In German), Monatsber, Berlin Akad., Germany, 1865.
69. H. A. Schwarz, *Gesammelte Matematische Abhandlungen* (In German), Springer, Berlin, 1980.
70. M. O'Keeffe, G. B. Adams and O. F. Sankey, Predicted new low energy forms of carbon, *Phys. Rev. Lett*. **68** (1992) 2325–2328.
71. W. M. Meier and D. H. Olson, *Atlas of Zeolite Structure Types*, 3rd ed., Butterworth-Heineman, London, UK, 1992.
72. E. Barborini, P. Piseri, P. Milani, G. Benedek and C. Ducati, Robertson Negatively curved spongy carbon, *J. Appl. Phys. Lett*. **81** (2002) 3359–3361.
73. G. Benedek, H. Vahedi-Tafreshi, E. Barborini, P. Piseri, P. Milani, C. Ducati and J. Robertson, The structure of negatively curved spongy carbon, *Diam. Relat. Mater*. **12** (2003) 768–773.
74. B. Szefler and M. V. Diudea, Polybenzene revisited, *Acta Chim. Slov* **59** (2012) 795–802.
75. M. V. Diudea and M. Petitjean, Symmetry in multi tori, *Symmetry Cult. Sci*. **19** (2008) 285–305.
76. B. Szefler and M. V. Diudea, Strain in Platonic fullerenes. *Struct. Chem* **25** (2014) 319–325.

77. M. V. Diudea and B. Szefler, Nanotube junctions and the genus of multi-tori, *Phys. Chem. Chem. Phys.* **14** (2012) 8111–8115.
78. B. Szefler and M. V. Diudea, Modeling tetrapodal nanotube junctions, *Comput. Methods Sci. Technol.* **18** (2) (2012) 111−115.