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Polybenzene multitori

Short Communication

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Abstract: Polybenzene unit BT_48 can dimerize either by identification of 8-membered rings to provide a diamond-like *fcc* net or by identifying the opening 12-membered rings to form intercalated dendrimer-dimers which can further grow and rather quickly superimpose over the diamond-like network. The third hypothetical moiety we consider here is an eclipsed isomer, that can form multitori as negatively curved structures of various complexity. Multitori can evolve spherically or show a linear periodicity, as in rods. The polybenzene ("armchair") multitori BTA are compared to the ("zig-zag") BTZ ones, proposed earlier by us. A graph-theoretical study related the structure of multitori to the genus of their embedding surface and established the lower and upper bound values of genus. The total energy per carbon atom, HOMO-LUMO gap and strain energy of BTA and BTZ multitori have been computed and the results obtained point to BTZ multitori to be at least as stable as C_{60} what suggests BTZ multitori can be eventually synthesized in laboratory.

Keywords: *Polybenzene • Multitorus • High genus surface • Linear periodic network*

1. Introduction

Multitori are complex structures consisting of more than one single torus [1-3]. They include negatively curved substructures [4-6], termed schwarzites, in honor of H. A. Schwarz [7,8], who firstly investigated the differential geometry of this kind of surfaces. Multitori probably result by self-assembly of some repeating units/monomers, formed by spanning of cages/fullerenes and can appear in spongy carbon and in natural zeolites, as well. Multitori can grow following either a spherical trend or a linear periodicity, in forming arrays of various complexity [9]. The high porosity of these materials could find applications in catalysis, gas and energy storage, gas and liquid purification, thermal insulation and in electrochemistry, as well.

The polybenzene [10] unit BT_48 dimerizes either by identification of octagons R(8) to provide a dimer named BDia2_88 and next a diamond-like *fcc*-net (Fig. 1, left column) or by identifying the "opening" rings R(12) when an "intercalated" dendimer-dimer BDen2_84 is formed, which can build the corresponding dendrimers: BDen5 at the first generation and BDen17 (Fig. 1, middle column) at the second generation. Further, any added unit will complete the diamond-like network over which the dendrimer is superimposed. A third way is an "eclipsed" isomer BTA2_90, its oligomers showing angles suitable to form structures of five-fold symmetry (Fig. 1, right column), eventually called multitori.

Multitori can be designed by appropriate map operations [9,11-15], as implemented in our original software CVNET [16] and Nano Studio [17].

Because of simplicity of the polybenzene and related structures, we try to bring here arguments in favor of attempts for their laboratory synthesis.

2. Theoretical details

2.1. Design of simple structures

The multitori bearing the benzene patch (see the polybenzene [10]) will have B as a prefix in their name. Next, because the opening faces show either "zig-zag" or "armchair" endings, "Z" or "A" will be added as a suffix to

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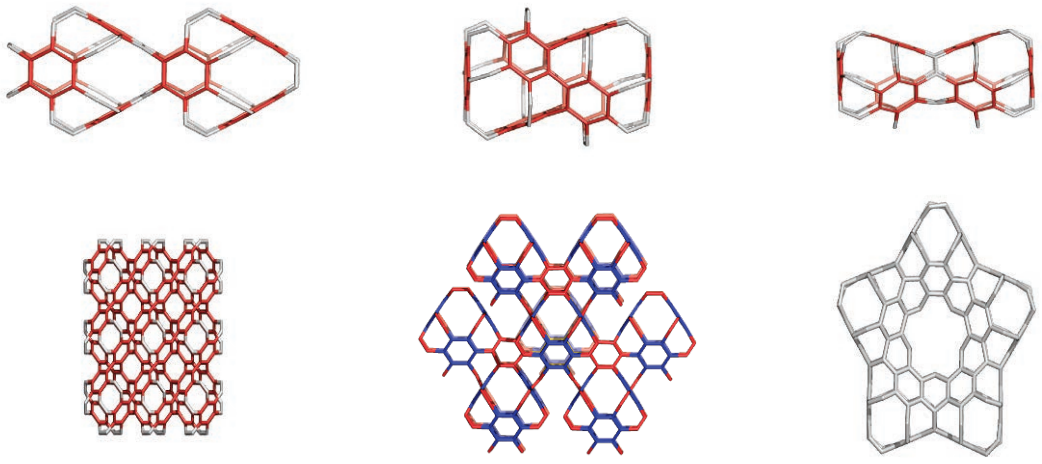

Figure 1. Top row: dimer-diamond-like BDia2_88 (left), dimer-dendrimer BDen2_84 (middle), dimer-multitorus BTA2_90 (right). Bottom row: Diamond-like net BDia_fcc(3,3,3)_864 (left), Dendrimer BDen17_ 624 (middle), Multitorus BTACy5_210, (right); the last numbers represent the atoms in molecule.

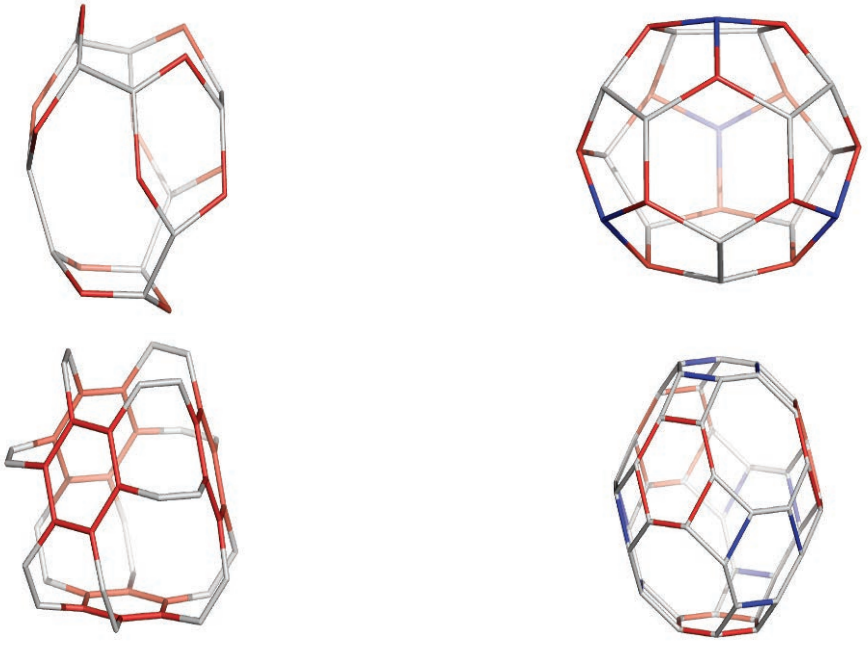

Figure 2. Top row: BTZ_24 designed from $S_2(T)\_28 = C_{28}$ by deleting the four blue points located at the centre of pentagon triples. Bottom row: BTA_48 formed by spanning the $Le(P_4(T))\_48$ cage following the blue bonds.

their name, as in BTZ or BTA. The number of repeating units and/or number of atoms will be added after the letters.

The design of simple units used to build up multi tori was made by using some operations on maps [11-15], applied on the Platonic solids. Fig. 2 illustrates the basic substructures of the two series: BTZ_24 and BTA_48, designed by spanning the corresponding cages, derived from the Tetrahedron T by map operations.

The dimers of BTA_48 and the hyper-ring BTACy5_210 were presented in Fig. 1. The unit BTZ_24, due to its simplicity, can form only the dimer leading to multitori, BTZ2_48 (not shown) and the corresponding five-fold hyper-ring BTZCy5_120 (also not shown).

2.2. Design of Multitori

The hyper-ring BTXCy5, (X=A, Fig. 1), can further evolve to the multitorus BTX17 (Fig. 3, top tow, left), the reduced graph of which is just C_{17} (Fig. 3, top tow, left),

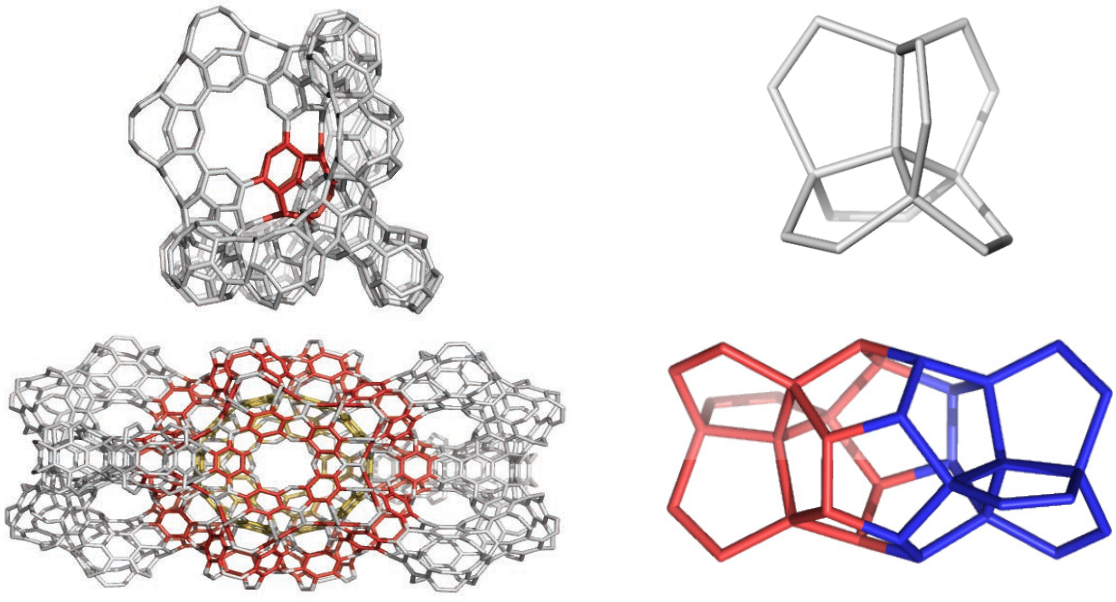

Figure 3. Top row: BTZ17_408 (left) and C_{17} (right); Bottom row: BTA34_1332 (right) and C_{34} (right).

the structure proposed by Diudea [18,19] as the seed for the diamond D_5. By analogy to D_5, a dimer BTX34 can be designed (Fig. 3, bottom row, left). It is noteworthy to mention that its reduced graph is C_{34} (Fig. 3, bottom row, right) the repeating unit [20] of the triple periodic structure of D_5.

The spherical multitorus BTX20 (the middle of structure, red/black - Fig. 3, right and Fig. 4, left column) is a *g*=21 multi torus, with a well-defined core: core(BTA20)_180=-f_5(*Le*$_{2,2}$(Do)), while core (BTZ20)_120=-d_5(S_2(Ico). In the above, -f_5 means deletion of all pentagonal faces in the transformed by Leapfrog (2,2) of the Dodecahedron Do, and d_5 is deletion of vertices of degree d=5, in the transform of Icosahedron=Ico by the septupling S_2 operation. Also, -d_5(S_2(Ico)=*Op*(*Le*(Ico)).

Recall, *g* is the genus of the surface where a structural graph is embedded and counts the number of simple tori ("handles") making that graph [21].

A linear array of BTX20, with the repeating unit formed by two units superimposing one pentagonal hyper-face (*i.e.*, BTXCy5), rotated to each other by an angle of PI/5 as in the "dimer" BTX20_2 (Fig. 5, top, left). Next, the structure can evolve with a one-dimensional periodicity, as shown in BTX20_4 (Fig. 5, top, right) or in the hyper-cycle BTZCy20_5_1800 (Fig. 5, bottom, left). Twelve units BTX20 can form a spherical array (of icosahedral symmetry), as in case of BTZSp20_12_3120, (Fig. 5, bottom, right), of which core is just BTZ20 (in fact a 13th unit).

Now we prove the following:

Theorem 1. *In multi tori built up from open tetrahedral units, the genus of structure equals the number of its units plus one*, *irrespective of the unit tessellation*.

Proof comes out from construction and is illustrated on the multitorus in Fig. 6: there are five tetrapodal units inserted into exactly five simple tori and all-together joined to the central, thus demonstrating the first part of the theorem.

For the second part, we apply the Euler's theorem [22]: $v-e+f=\chi=2(1-g)$,
where $v=|V(G)|$ is the number of vertices/atoms, $e=|E(G)|$, the number of edges/bonds and *f* is the number of faces of the graph/molecule. In the above, *g* is the *genus* of the (orientable) surface *S* on which a molecular graph is embedded, *i.e.*, *g* is the number of "handles" in the structure.The genus is related to the Gaussian curvature of the surface *S* by means of Euler's characteristic χ of *S* (Gauss-Bonnet theorem [23,24]) as: for *g*=0 (case of sphere) χ >0 (positive curvature); for *g*=1 (case of torus) χ =0 while for *g*>1 (surfaces of high genera), χ <0 , S shows a negative curvature. More about surfaces of negative curvature the reader can find in [1,2]. To complete the demonstration, data in Table 1 provide the values of *g* in several BTX multi tori, tessellation differing as X=A or Z.

The number of tetrahedral units BTX1 in the linear array of BTX20_*k* (Table 1, entries 3 to 6) is *u*=20*k*-5(*k*-1)=15*k*+5, according to the construction mode. The term -5(*k*-1) accounts for the superimposed hyper-rings BTXCy5. In case of BTZCy20_5, (Table 1,

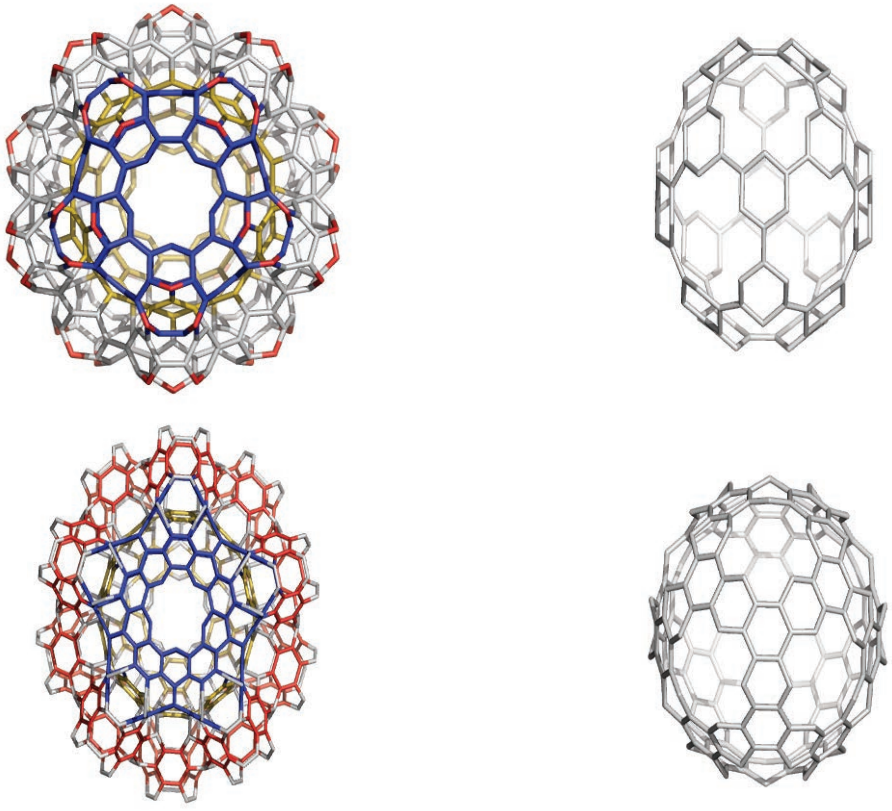

Figure 4. Top row: multi torus BTZ20_1_480 (left) and its core_120 (right). Bottom row: multi torus BTA20_1_780 (left) and its core_180 (right) .

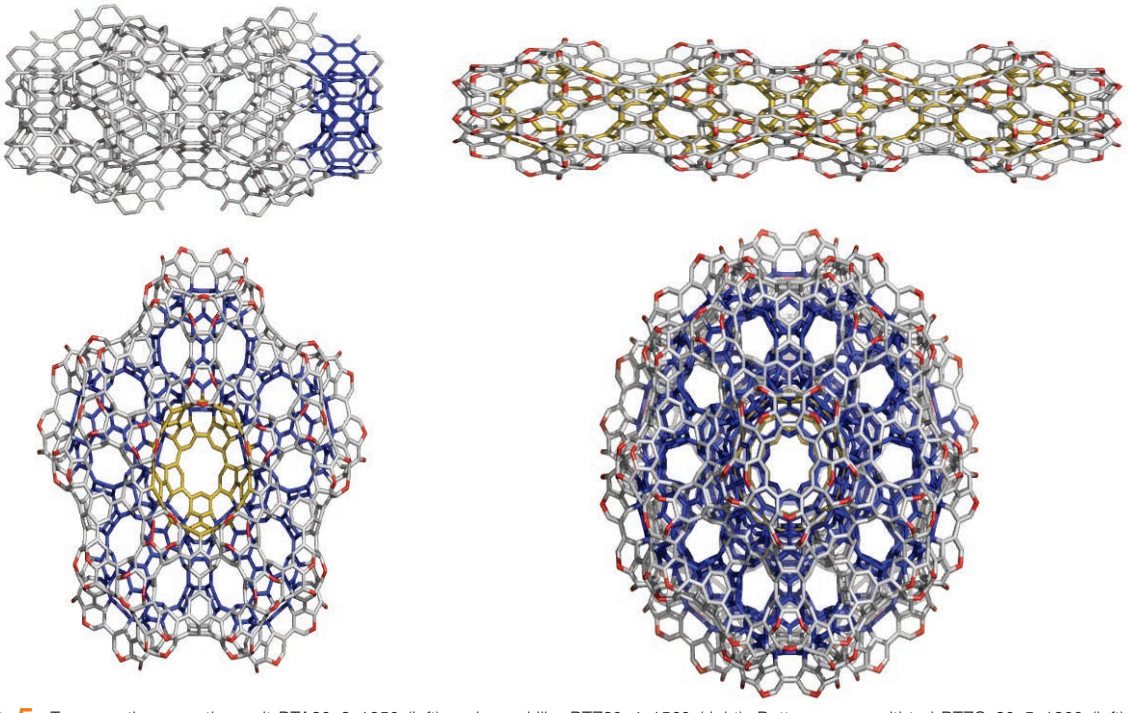

Figure 5. Top row: the repeating unit BTA20_2_1350 (left) and a rod-like BTZ20_4_1560 (right). Bottom row: multi tori BTZCy20_5_1800 (left) and BTZSp20_12_3120 (five-fold symmetry).

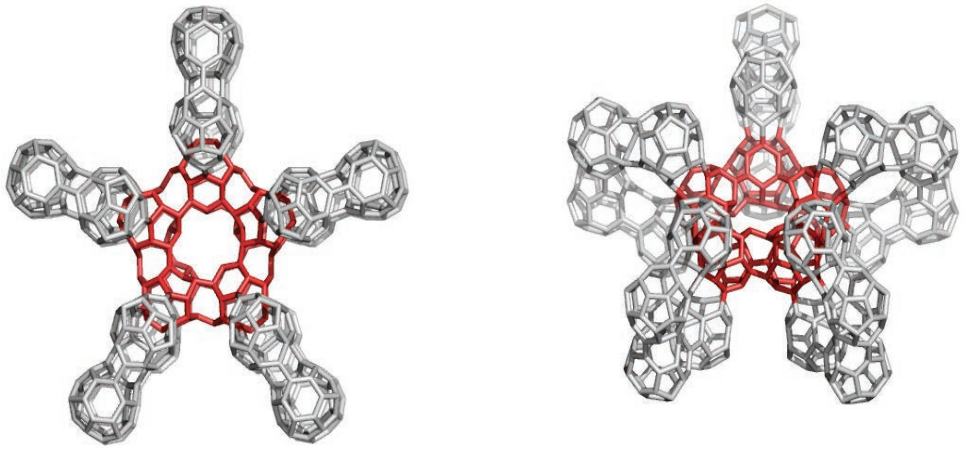

Figure 6. BTZCy5: five tetrapodal units (each closing its own ring) joined at the central ring, thus the genus is calculated g=5+1.

Table 1. Euler formula calculation in multi tori BTX.

	BMTX	v	e	f_6	f_8	f_{tot}	2(1-g)	g	u	u-formula
1	BTACy5	210	285	35	30	65	-10	6	5	$f_8/6$
2	BTZCy5	120	165	20	15	35	-10	6	5	$f_6/4$
3	BTA20_1	780	1110	170	120	290	-40	21	20	$f_8/6$
4	BTZ20_1	480	690	80	90	170	-40	21	20	$f_6/4$
5	BTA20_5	3060	4410	710	480	1190	-160	81	80	$f_8/6$
6	BTZ20_5	1920	2790	320	390	710	-160	81	80	$f_6/4$
7	BTZCy20_5	1800	2625	300	375	675	-150	76	75	$f_6/4$
8	BTZ20_12	4440	6465	740	915	1655	-370	186	185	$f_6/4$
9	BTZSp20_12	3120	4590	520	690	1210	-260	131	130	$f_6/4$

Table 2. Total energy E_{tot} per Carbon atom and HOMO-LUMO HL Gap, at Hartree-Fock HF level of theory and Strain energy according to POAV theory in benzene-patched structures vs C_{60} taken as the reference.

	Structure	E_{tot}/(au)	E_{tot}/C (au)	HL Gap (eV)	Strain/C (kcal mol^{-1})
1	BTA_48	-1831.484	-38.156	11.285	0.083
2	$BTA_{Cy,5}$–210	-7986.806	-38.032	9.545	0.392
3	BTZ_24	-915.092	-38.129	8.221	7.614
4	$BTZ_{Cy,5}$–120	-4558.826	-37.990	7.178	4.893
5	C_{60}	-2271.830	-37.864	7.418	8.256

entry 7) formula is u=20k-5k=15k, k=5, the last hyper-ring unit being omitted because of the cyclic structure. Thus, the drop in g is of 5 units for each five-fold hyper-cycle (compare Table 1, entries 6 and 7).

In case of the spherical array BTZSp20_12 (Table 1, entry 9), u=20k-2[5(k-1)], k=12. Remark the twice subtraction of the term 5(k-1), in case of the spherical array, which accounts for the difference in g to the linear array of k=12 (Table 1, entries 8 and 9): 186-131=55=5(12-1). This drop in g, in case of the spherical array, seems to parallel the well-known result that sphere is the minimal surface among all known solid objects. The number u is also related to the number of faces as: $u = f_8/6$ in case BTA and $u = f_6/4$ in case BTZ.

On the ground of Theorem 1, the spherical array BTZSp20_12 seems to be the *minimum g* (lower bound) while BTZ20_k *maximum g* (upper bound) among all the studied structures. We demonstrated the following:

Theorem 2. *The genus in multi tori shows the lower bound value in structures of icosahedral symmetry while the upper bound value is shown in linear structures, provided the same number of* (*open*) *tetrahedral units*.

Carbon atom **orbit analysis** in BTZSp20_12 revealed a 6.8^2 massive class (2580 atoms, about 83%), located inside, of the same signature as in polybenzene [10], and two smaller classes, of signature 6.8 (360 atoms), and 6 (180 atoms), disposed outside the spherical structure. Compare with % of 6.8^2 in the linear array BTZ20_*k* (about 74% at *k*=12) and in BTA20_*k* (about 26%, at *k*=9). Knowing the (calculated [24]) stability of polybenzene, consisting of only 6.8^2 atoms (in the infinite triple periodic net), the orbit analysis can be seen as a "topological proof" of stability of the spherical array BTZSp20_12.

2.3. Stability of nanotube junctions

The test of stability was done to support the idea that the basic substructures of multitori could appear in real experiments, by self-assembly of some very simple repeating units. Data are listed in Table 2, taking C_{60} as the reference structure.

Total energy per carbon atom, calculated at the Hartree-Fock HF level of theory and the HOMO-LUMO gap as well, show the BTA_48 and its derived hyper-pentagon the most stable structures in Table 2. The Strain energy, calculated according to the Haddon's POAV theory [25,26] is also in favor of BTA-substructures and is far less than in case of the closed cage C_{60}. Table 2 suggests the benzene-patched as being possible candidates to real molecules eventually self-assembled in more complex multitori as exist in spongy-carbon or zeolites.

3. Computational details

The structures, as finite hydrogen-ended ones, were optimized at the Hartree-Fock HF (HF/6-31G**) level of theory. The calculations were performed in gas phase by Gaussian 09 [27]. The single point energy minima obtained for the investigated structures were collected in Table 2. Strain energy values were computed by JSChem program [28]. Operations on maps were made by our CVNET program [16] while the topological analysis was done by Nano Studio software package [17].

4. Conclusions

Polybenzene unit BT_48 was shown to dimerize either by identification of octagons R(8) to provide the diamond-like *fcc*-net or by identifying the "opening" rings R(12) when the "intercalated" dendrimer-dimer will finally superimpose over the diamond-like network. A third way was shown to be an "eclipsed" isomer, the oligomers of which form structures of five-fold symmetry, called multitori.

A rational structure construction was given for the multitori herein considered and for some of their subunits, as well. The polybenzene "armchair" BTA multitori were compared to the "zig-zag" BTZ, previously proposed at the TOPO Group Cluj.

It is worthy to note that the BTZ structures are the most simple patched nanostructures, consisting of atoms only forming isolated benzene rings. Their stability was found to be at least that of C_{60} and this could be a promise for their laboratory synthesis.

A graph-theoretical study related the structure of multitori to the genus of their embedding surface and established the lower and upper bound genus values.

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