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Dedicated to Costică MUSTĂŢA on his 60[th] anniversary

PERIODIC 4,7 CAGES

Mircea V. DIUDEA

Abstract. A constructive procedure for 4,7 trivalent cages and their corresponding fused periodic cages are given. A counting theorem for these structures is formulated in terms of a general counter and of a periodic description.

Introduction.

Pure carbon cages, with the best studied spherical fullerenes and capped tubulenes, represent novel allotropes of the carbon, generically called nanostructures.[1-5] Carbon is unique by the variety of its stable forms: chains, rings and cages, involving two, three and four coordination.

A polyhedron having v vertices, e edges and f faces, obeys the Euler's theorem:[6]

$$v - e + f = \chi(S) \tag{1}$$

with $\chi(S)$ being the Euler's characteristic of the closed smooth surface S on which the polyhedron is embedded. Formula is useful for checking the consistency of an assumed structure. In this respect, other two results, also due to Euler, are recalled:[7]

$$\sum_d d v_d = 2e \tag{2}$$

$$\sum_s s f_s = 2e \tag{3}$$

where v_d and f_s denote vertices of degree (*i.e.*, valency) d and s sided faces, respectively.

It is generally agreed that introduction of a small-sized cycle into a map (*i.e.*, a lattice) covering a closed surface will produce a positive local curvature (and implicitly a strain, correlated with increased energy - when the system is a chemical one). Contrarily, a larger-sized cycle will bear a negative curvature. The total Gaussian curvatures[8,9] k on a surface S represent a topological invariant (Gauss-Bonnet theorem):

$$\int_S k\,dA = 2\pi\chi(S) \tag{4}$$

For S being the sphere, $\chi(S)$ is 2 while for the torus and cylinder is 0.

An Euler characteristic per site can be formulated as:[6,10]

$$\sum_j (6-j) f_j = \chi_i \qquad (5)$$

where summation runs over all j-fold cycles surrounding the vertex i. Thus, the combinatorial curvature CK can be given in terms of χ_i :

$$CK = \frac{1}{v} \sum_i \chi_i \qquad (6)$$

This paper proposes a way of building 4,7 trivalent cages and their corresponding fused periodic cages, for which a counting theorem is formulated in terms of a general and of a periodic counter.

Construction of 4,7 Cages

A cage built up only of 4-fold and 7-fold faces can be obtained in the following way: A tube TUHPH [9,4][11] (*i.e.*, a covering consisting of 6, 4, 6, 4-fold faces, disposed as bracelets, and next joined to form a tube, embedded on the cylinder - Figure 1, a) is cut as shown in (b) and next joined by a twist-coupling TW1 procedure (c). In the next step (d) 7-fols faces (12 points) are added at the two ends of the structure (c). From (d), 12 points are deleted to obtain (e) and next, by a TW3 and identifying the opposite points (*i.e.*, deleting 6 points) results in structure (f). Finally, the structures (d) and (f) are capped by adding one point at each of their open ends to give the target structures CA_4,7 (26 points) and CB_4,7, (44 points).

Fulleroid cages of 5,7 type were reported in ref. 12.

TUHPH [9,4] ; (a) (36 points) (b) (a-6 ; 30 points)

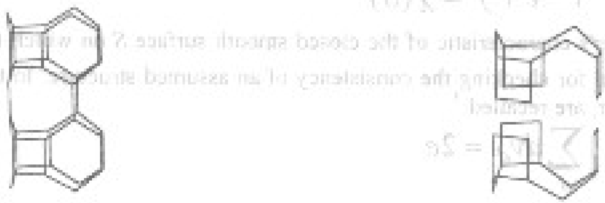
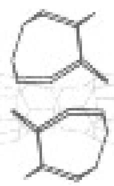


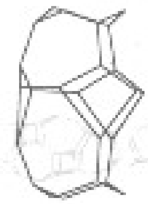
Figure 1. Construction algorithm for the 4,7 trivalent cages of series A and B.

(c) (b_TW1 ; 30 points) (d) (c+12; 42 points)

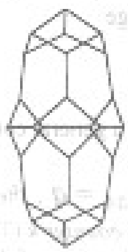
(e) (d-12; 30 points) (f) (e-6_TW3 ; 24 points)



CA_4,7; (26 points)



CB_4,7; (44 points)



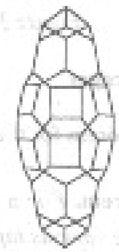
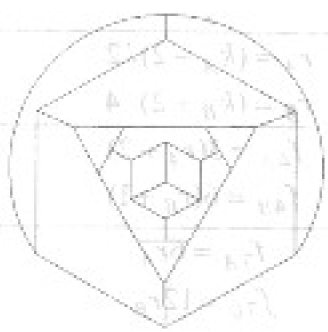


Figure 1. (continued)

The first terms of the series A and B, illustrated in Figure 1 are 4,7 cages embedded on the sphere. As a consequence, they can be depicted by their Schlegel projection (Figure 2).

CA_4,7



CB_4,7

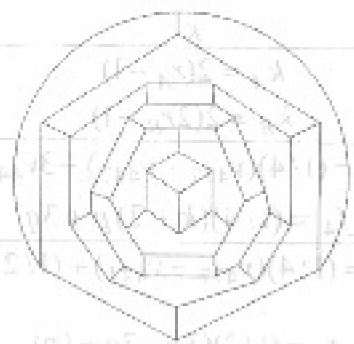


Figure 2. Schlegel projection of the monomeric 4,7 cages

In a further step, two uncapped units (see Figure 3) are joined by identifying their opposite edges to give a periodic 4,7 cage (in our example B_2_4,7).

(2(b1_47-6)) B$_2$_4,7 (80 points)

Figure 3. Building of a dimeric periodic 4,7 cage

Counting 4,7 cages

A counting theorem for these structures is formulated in terms of a general counter and of a periodic description:

Cage 4,7 Typing Theorem. *For a cage 4,7 having* $e_{44} = p$ *and* $v_{444} = q$ *, the number of faces, edges, and vertices of the various types can be counted as a function of the counter k* (Table 1, column k). *If the cages are periodic structures, the type counting can be made as a function of the repeating unit r* (Table 1, column *r*).

Table 1. Periodic Cages 4,7

	K	*r*
1	$k_A = 2(r_A - 1)$ $k_B = 2(2r_B - 1)$	$r_A = (k_A + 2)/2$ $r_B = (k_B + 2)/4$
2	$f_4 = (1/4)(v_{477} - v_{447}) + 3v_{444}$ $f_4 = (1/4)(k+2)p + 3q$	$f_{4A} = 3(r_A + 2)$ $f_{4B} = 6(r_B + 1)$
3	$f_7 = (1/4)(v_{477} + v_{447}) + (1/2)v_7$ $f_7 = (1/2)(3p - 3q + kp)$	$f_{7A} = 6r_A$ $f_{7B} = 12r_B$

4	$e_{44} = p$ $e_{47} = (4+k)p$ $e_{77} = 4p - (15/2)q + (5/4)pk$	$e_{44} = p$ $e_{47A} = 2(r_A + 1)p$ $e_{47B} = 2(2r_B + 1)p$ $e_{77A} = (3/2)p - (15/2)q + (5/2)pr_A$ $e_{77B} = (3/2)p - (15/2)q + 5pr_B$
5	$v_{444} = q$ $v_{447} = 2p - 3q$ $v_{477} = (k+4)p - 3q$ $v_{777} = kp/2$	$v_{444} = q$ $v_{447} = 2p - 3q$ $v_{477A} = 2(r_A + 1)p - 3q$ $v_{477B} = 2(2r_B + 1)p - 3q$ $v_{777A} = (r_A - 1)p$ $v_{777B} = (2r_B - 1)p$
6	$N = 6p - 5q + (3/2)pk$	$N_A = 3p(r_A + 1) - 5q$ $N_B = 3p(2r_B + 1) - 5q$
7	$k_m = k_A + k_B + 2$ $k_m = 2(r_A + 2r_B - 1)$	$r_A = (1/2)k_m - 2r_B + 1$ $r_B = ((1/2)k_m - r_A + 1)/2$
8	$f_{4m} = (1/4)(k_m + 2)p + 3q$ $f_{7m} = (1/2)(3p - 3q + k_m p)$	$f_{4m} = f_{4A} + f_{4B} - 6$ $f_{7m} = f_{7A} + f_{7B}$
9	$N_m = 6p - 5q + (3/2)pk_m$	$N_m = N_A + N_B - 8(r_A + r_B - 1)$ $N_m = r_A N_{1A} + r_B N_{1B} - 8(r_A + r_B - 1)$

The above theorem is demonstrated by construction (see also ref. 6). It also hold in mixed cages, (Table 1, entries 7 to 9). Table 2 includes the counting results for some cages 4.7. It is easily seen that these cages have predominant negative curvature (column *CK*, Table 2).

Table 2. Counting Results in Some Cages 4,7.

	Cage	k	r	4	7	$e_{4,4}$	$e_{4,7}$	$e_{7,7}$	$v_{4,4,4}$	$v_{4,4,7}$	$v_{4,7,7}$	$v_{7,7,7}$	CK
1	$C3A_{\_4,7}$ N = 26; E = 39	0	1	9	6	6	24	9	2	6	18	0	1.154
2	$C3A_{2\_4,7}$ N = 44, E = 66	**2**	**2**	**12**	**12**	**6**	**36**	**24**	**2**	**6**	**30**	**6**	**0.273**
3	$C3A_{3\_4,7}$ N = 62; E = 93	4	3	15	18	6	48	39	2	6	42	12	-0.097
4	$C3A_{4\_4,7}$ N = 80; E = 120	6	4	18	24	6	60	54	2	6	54	18	-0.387
5	$C3B_{\_4,7}$ N = 44; E = 66	**2**	**1**	**12**	**12**	**6**	**36**	**24**	**2**	**6**	**30**	**6**	**0.273**
6	$C3B_{2\_4,7}$ N = 80; E = 120	6	2	18	24	6	60	54	2	6	54	18	-0.300
7	$C3B_{3\_4,7}$ N = 116; E = 174	10	3	24	36	6	84	84	2	6	78	30	-0.517
8	$C3AB_{\_4,7}$ N = 62; E = 93	4	-	15	18	6	48	39	2	6	42	12	**-0.097**
9	$C3AAB_{\_4,7}$ $C3ABA_{\_4,7}$ N = 80; E = 120	6		18	24	6	60	54	2	6	54	18	-0.300
10	$C3ABB_{\_4,7}$ N = 98; E = 147	8	-	21	30	6	72	69	2	6	66	24	-0.429

Perspectives

The cutting-coupling procedure above suggested could be important in the fullerene synthesis, where incompletely formed cages were observed. They may join together to form supramolecular assemblies.[13] If the joining units are identical, it results in a pure polymeric structure, or, in mathematical sense, a periodic structure.[14] If the units are different , the resulting structure is called a co-polymer. The joining unit can also be variable, consisting *e.g.*, of pure 7 rings (Figure 4, a) or mixed 5,7 rings (Figure 4, b).

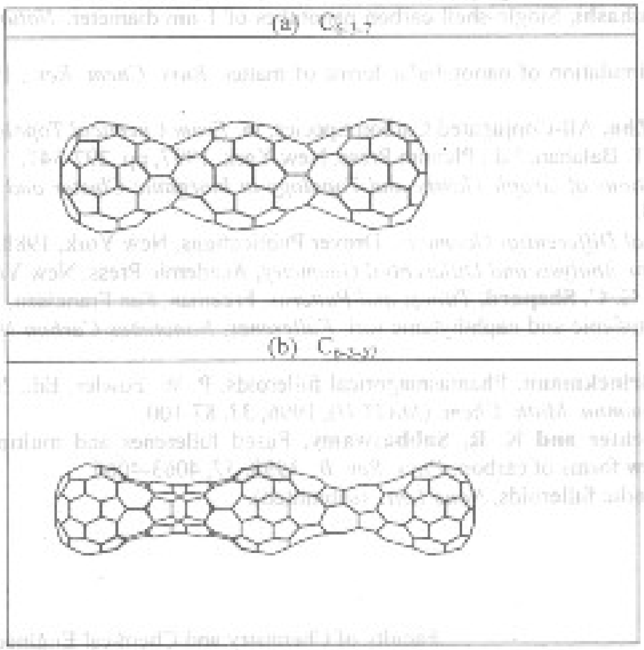


Figure 4. Periodic fullerenes with the repeating unit $r = 3$ and joining units 7 (a) and 5,7 (b).

Conclusions

Pure 4,7 trivalent cages were built up by using small segments of the tubular HPH net and appropriate cutting-joining operations. Such transformations could be plausible routes in the fate of the vaporized graphite.

Counting of the constitutive components of the 4,7 cages was accomplished in terms of a general counter and of a periodic description.

The novel class of periodic fullerenes, announced here, showed a heat of formation lower than the parent spherical fullerenes,[14] deserving more attention in theoretical studies and experimental research.

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Faculty of Chemistry and Chemical Engineering
Babes-Bolyai University, 3400 Cluj, Romania