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ORIGINAL PAPER

Tubercular fulleroids

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Abstract New tubercular fulleroids are built up by using the three classical composite map operations: tripling (leapfrog *Le*), quadrupling (chamfering *Q*) and septupling (capra *Ca*) on the trivalent Platonic solids. These transforms belong to the tetrahedral, octahedral and icosahedral symmetry groups and show interesting mathematical and (possible) physico-chemical properties.

Keywords Fullerenes · Map operations · Leapfrog · Chamfering · Capra · Opening operation · Kekulé valence structure · Kekulé structure count

1 Introduction

A map M is a combinatorial representation of a closed surface [1]. Several transformations (i.e., operations) on maps are known and used for various purposes.

Let us denote in a map: v, number of vertices; e, number of edges; f, number of faces; and d, vertex degree. A subscript "0" will mark the corresponding parameters in the parent map.

Recall some basic relations in a map [2]:

$$\sum dv_d = 2e \tag{1}$$

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$$\sum s f_s = 2e \tag{2}$$

where v_d and f_s are the number of vertices of degree d and number of s-gonal faces, respectively. The two relations are joined in the famous Euler [3] formula:

$$v - e + f = \chi(M) = 2(1 - g) \tag{3}$$

with χ being the Euler *characteristic* and g the genus [4] of a graph (i.e., the number of handles attached to the sphere to make it homeomorphic to the surface on which the given graph is embedded; $g = 0$ for a planar graph and 1 for a toroidal graph). Positive/negative χ values indicate positive/negative curvature of a lattice. This formula is useful for checking the consistency of an assumed structure.

The article is organized as follows: the second section gives definitions and illustrations of the main map operations used within this work. The third section presents the opening operations leading to the tubercular structures by appropriate capping. The forth section gives a method for computing the number of Kekule valence structures of the discussed tubercular cages. Conclusions, references and an appendix will close the article.

2 Operations on maps

Dualization Du of a map starts by locating a point in the center of each face (Fig. 1a) [1,5]. Next, two such points are joined if their corresponding faces share a common edge (Fig. 1b).

It is the (Poincaré) *dual Du*(M). The vertices of $Du(M)$ represent the faces of M and vice-versa [1]. Thus the following relations exist:

$$Du(M) : v = f_0;\ e = e_0;\ f = v_0 \tag{4}$$

Dual of the dual returns the original map: $Du(Du(M)) = M$. Tetrahedron is self dual while the other Platonic polyhedra form pairs: *Du*(Cube) = Octahedron; *Du*(Dodecahedron) = Icosahedron (Fig. 2). It is also known the Petrie dual [1].

Polygonal P_r capping ($r = 3, 4, 5$) of a face is achieved as follows [6]: add a new vertex in the center of the face. Put r-3 points on the boundary edges (Fig. 3). Connect

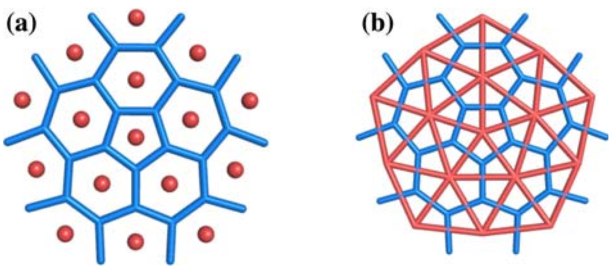


Fig. 1 Dualization of a fullerene patch

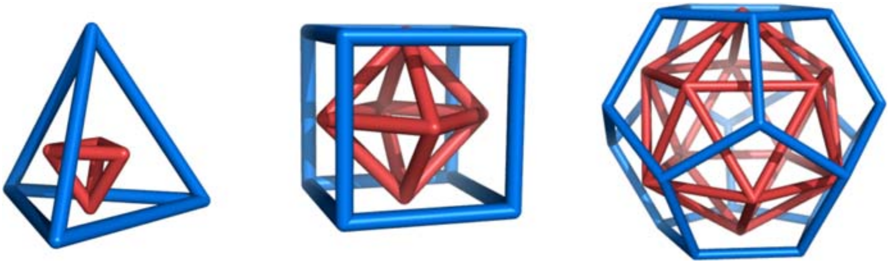


Fig. 2 The duals of the five Platonic polyhedra

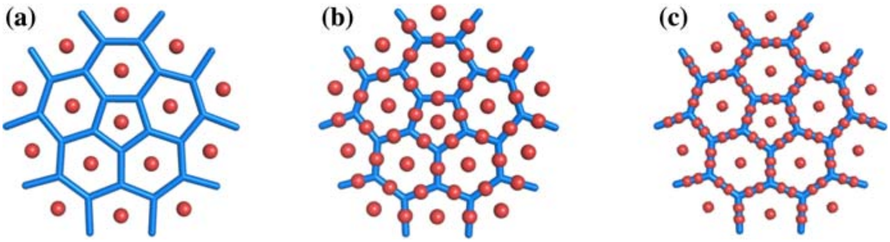


Fig. 3 Polygonal capping of a fullerene patch; P_3 (**a**); P_4 (**b**); and P_5 (**c**)

the central point with one vertex (the end points included) on each edge. In this way the parent face is covered by triangles ($r = 3$), quadrilaterals ($r = 4$) and pentagons ($r = 5$). The P_3 operation is also called *stellation* or (centered) *triangulation*. When all the faces of a map are thus operated, it is referred to as an omnicapping P_r operation (see Fig. 4). The resulting map shows the relations:

$$P_r(M)\colon v = v_0 + (r-3)e_0 + f_0; \quad e = re_0; \quad f = s_0 f_0 \tag{5}$$

so that the Euler's relation holds.

Maps transformed by the above operations form dual pairs:

$$Du(P_3(M)) = Le(M) \tag{6}$$

$$Du(P_4(M)) = Me(Me(M)) \tag{7}$$

$$Du(P_5(M)) = Sn(M) \tag{8}$$

Vertex multiplication ratio by this dualization is always:

$$v(Du)/v_0 = d_0 \tag{9}$$

Relations (6) to (8) enable the construction of Archimedes/Catalan objects, when applied on the Platonic solids [1,7]. The appearing operations will be detailed below. Equation 11 comes out from: $v(Du) = f(P_r(M)) = s_0 f_0 = d_0 v_0$ (Eqs. 4 and 5).

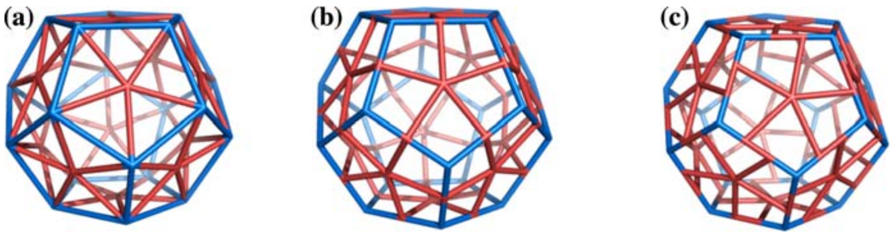


Fig. 4 Polygonal capping of the Dodecahedron by $P_3(D)$ (**a**); $P_4(D) = (C_{10})^*$ (**b**); and $P_5(D) = (C_9)^*$ (**c**) (*) Symbols in the brackets are identical to those used in De La Vaissiere et al. [7] for Catalan objects (i.e., duals of the Archimedean solids); for other naming of the operations see HART (2004)

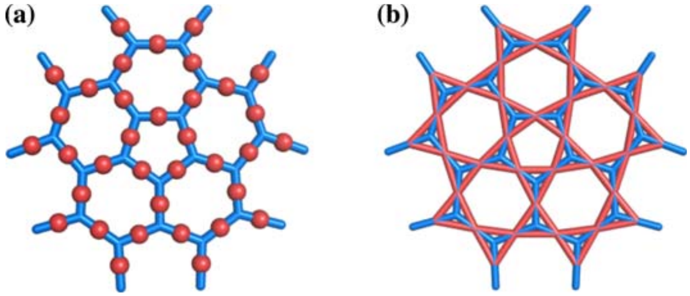


Fig. 5 Medial of a fullerene patch

Note that all the operation parameters herein presented refer to regular maps (i.e., having all vertices and faces of the same valence/size). Figure 4 gives examples of the P_r operations realization.

Medial Me of a map is achieved[1] by putting a new vertex in the middle of each original edge (Fig. 5a). Join two vertices if the original edges span an angle (and are consecutive within a rotation path around their common vertex in M). Medial is a 4-valent graph and $Me(M) = Me(Du(M))$, as illustrated in Fig. 5b.

The transformed parameters are:

$$Me(M)\colon v = e_0; \quad e = 2e_0; \quad f = f_0 + v_0 \tag{10}$$

Medial operation rotates parent s-gonal faces by π/s. Points in the medial represent original edges, thus this property can be used for topological analysis of edges in the parent polyhedron. Similarly, the points in dual give information on the topology of parent faces. Figure 6 illustrates the *medial* operation performed on the five Platonic polyhedra.

Truncation Tr is achieved[1] by cutting off the neighborhood of each vertex by a plane close to the vertex, such that it intersects each edge incident to the vertex (Fig. 7).

Truncation is similar to the medial, the transformed parameters being:

$$Tr(M)\colon v = 2e_0 = d_0 v_0; \quad e = 3e_0; \quad f = f_0 + v_0 \tag{11}$$

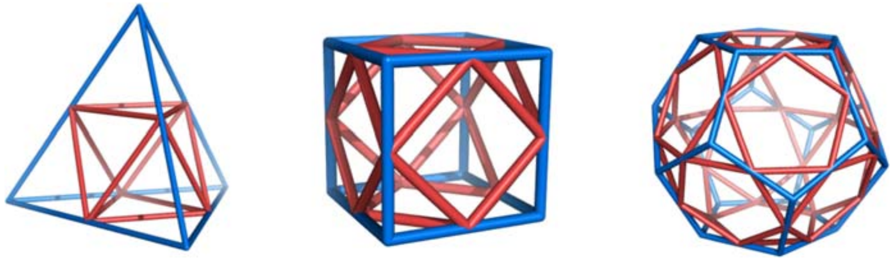


Fig. 6 The medials of the five Platonic polyhedra

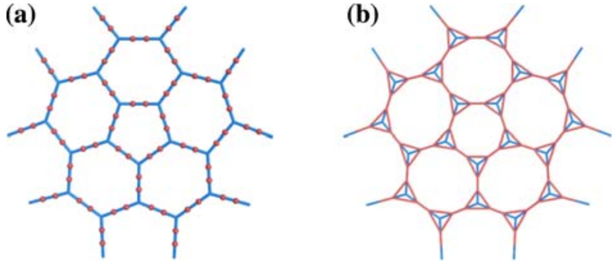


Fig. 7 Truncation of a patch of a fullerene

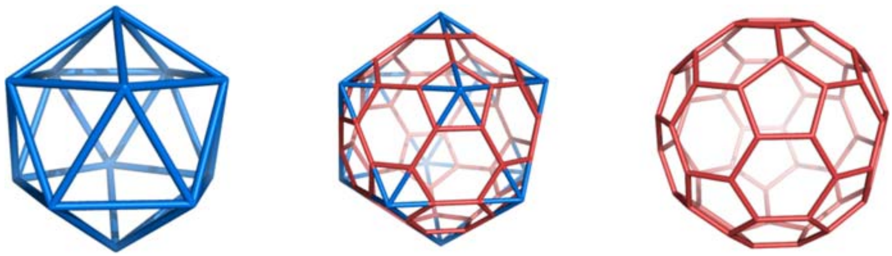


Fig. 8 The truncation of the Icosahedron

This was the main operation used by Archimedes in building up the well-known 13 solids [7]. Figure 8 illustrates the realization of this operation on the icosahedron.

Snub Sn is a composite operation that can be written as [6]:

$$Sn(M) = Dg(Me(Me(M))) = Du(P_5(M)) \tag{12}$$

where Dg means the inscribing diagonals[1] in the quadrilaterals resulting by $Me(Me(M))$. The true dual of the snub is the $P_5(M)$ transform: $Du(Sn(M)) = P_5(M)$. Similar to the medial operation, $Sn(M) = Sn(Du(M))$. In case of $M = T$, the snub $Sn(M) = I$.

Of chemical interest is the easy transformation of the snub (i.e., regular pentavalent graph) into the leapfrog transform (i.e., regular trivalent graph—see below), by deleting the edges of the triangle joining any three parent faces (Fig. 9, in black). This is particularly true in the snub of trivalent parent maps.

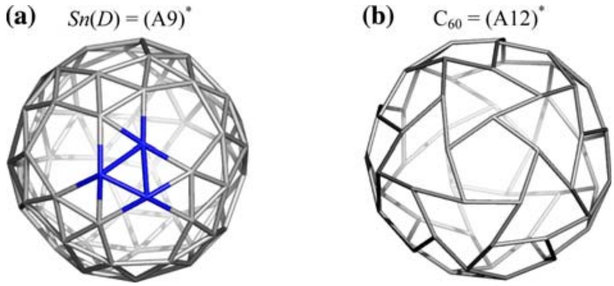


Fig. 9 Snub of Dodecahedron; * Symbols in the brackets are identical to those used in ref. [7] for the Archimedean solids

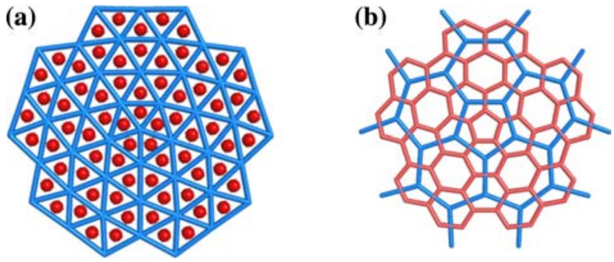


Fig. 10 Stellation (**a**) and dualization (**b**) of a patch of a fullerene

The transformed parameters are:

$$Sn(M)\colon v = s_0 f_0 = d_0 v_0; \quad e = 5e_0; \quad f = v_0 + 2e_0 + f_0 \tag{13}$$

The multiplication ratio is $v/v_0 = d_0$, the same as for $Le(M)$, both of them involving the dualization (see below).

Leapfrog Le is a composite operation [8–12] which can be written as:

$$Le(M) = Du(P_3(M)) = Tr(Du(M)) \tag{14}$$

A sequence of stellation (i.e., P_3)-dualization rotates the parent s-gonal faces by π/s. Leapfrog operation is illustrated, for a fullerene patch, in Fig. 10.

Quadrupling Q (i.e., chamfering [13]) is another composite operation, achieved by the sequence [6]:

$$Q(M) = E_{-}(Tr_{P_3}(P_3(M))) \tag{15}$$

where E_{-} means the (old) edge deletion (the blue lines, in Fig. 11) of the truncation Tr_{P_3} of each central vertex introduced by P_3 capping. Q insulates the parent faces always by hexagons.

Capra Ca—the goat, is the Romanian corresponding of the *leapfrog* English children game. It is a composite operation [6,14,15] necessarily coming from the Goldberg's [13] multiplying factor m:

$$m = (a^2 + ab + b^2); \quad a \geq b; \quad a + b > 0 \tag{16}$$

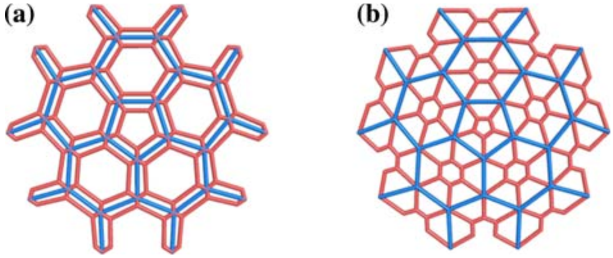


Fig. 11 Chamfering of a patch of a fullerene

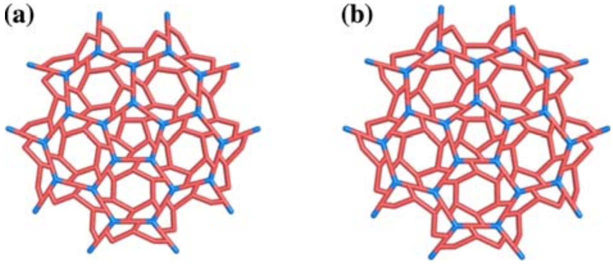


Fig. 12 Chiral lattices performed by the capra *Ca* operation

that predicts m (in a 3-valent map) as follows: *Le*: (1, 1); $m = 3$; Q: (2, 0); $m = 4$; *Ca*: (2, 1); $m = 7$.

The transformation can be written as [6,15]:

$$Ca(M) = Tr_{P_5}(P_5(M)) \tag{17}$$

with Tr_{P_5} meaning the truncation of each central vertex introduced by P_5 capping. *Ca* insulates any face of M by its own hexagons, which are not shared with any old face (in contrast to *Le* or Q). It is an intrinsic chiral operation (it rotates the parent edges by $\pi/(3s/2)$—Figs. 12, 13).

The operation is illustrated in Fig. 13, along with *Le* and Q ones; the cages are also given in the Schlegel projection [16]. Note that *Ca* is S_1 operation, differing from its S_2 twin operation [15].

3 Opening operation

The above operations $\Omega(M)$ can continue by an E_n homeomorphic transformation $E_n(\Omega(M))$ of the boundary edges of the parent-like faces thus resulting open maps with all polygons of the same size. In case of E_1 operation the size is: 9 (*Le*); 8 (Q) and 7 (*Ca*). This opening transformation is illustrated in Fig. 14 in the case of dodecahedron D.

The opening faces by E_1 operation are "zig-zag" tubule junctions. They can be further capped by all-pentagon caps C_5, as illustrated in Fig. 15 and also in Appendix.

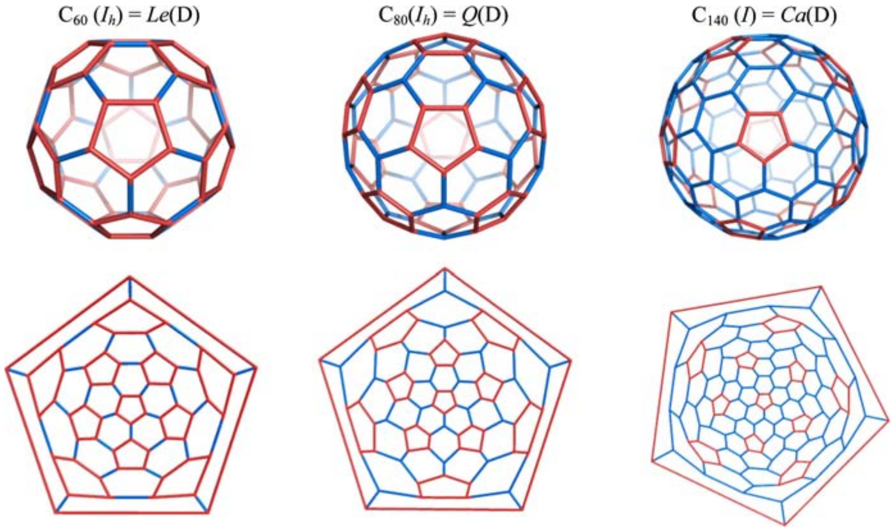


Fig. 13 Molecular realization of the three main composite map operations, given both as 3D objects and Schlegel projections (the bottom row)

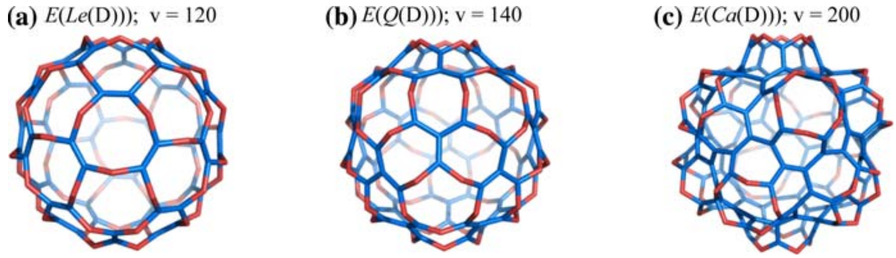


Fig. 14 Opening of the Dodecahedron D transformed by: leapfrog *Le*, quadrupling *Q* and capra *Ca*

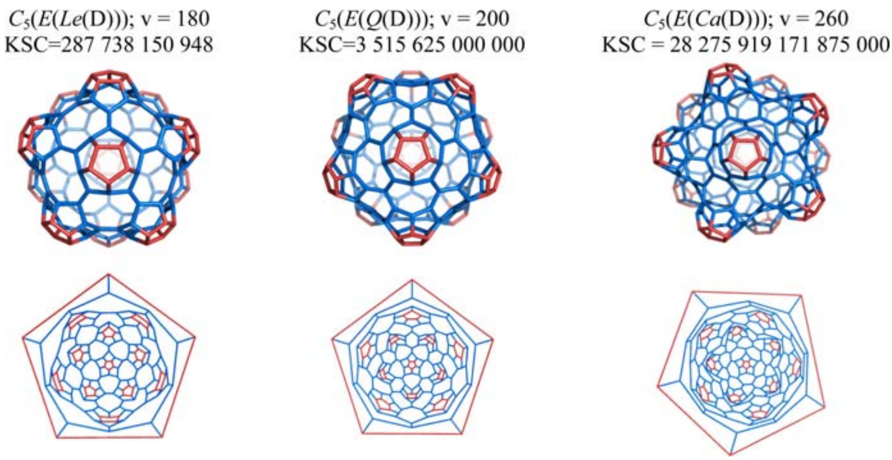


Fig. 15 Capping by C_5 Dodecahedron "halves" of the open Dodecahedron transformed by: *Le, Q* and *Ca*, given both as 3D objects and Schlegel projections (the bottom row)

Table 1 Parameters of simple Hückel theory in cages $C_5(E(\Omega(\mathrm{D})))$ and their leapfrog transforms

	Cage	v	Homo −2	Homo −1	Homo	Lumo	Lumo +1	Lumo +2	Gap	x_+	x_0	x_-
1	$C_5(E(Le(\mathrm{D})))$	180	0.380	0.380	0.380	0.257	0.257	0.257	0.123	96	0	84
2	$Le(C_5(E(Le(\mathrm{D}))))$	540	0.242	0.242	0.198	0.198	0.198	0.198	0.000	220	1	199
3	$C_5(E(Q(\mathrm{D})))$	200	0.425	0.425	0.311	0.311	0.311	0.311	0.000	103	4	93
4	$Le(C_5(E(Q(\mathrm{D}))))$	600	0.457	0.457	0.457	−0.171	−0.171	−0.171	0.628	300	0	300
5	$C_5(E(Ca(\mathrm{D})))$	260	0.385	0.385	0.287	0.287	0.287	0.287	0.000	133	0	127
6	$Le(C_5(E(Ca(\mathrm{D}))))$	780	0.294	0.294	0.294	−0.172	−0.172	−0.172	0.466	390	0	390
7	Dress	260	0.238	0.238	0.077	0.077	0.077	0.077	0.000	133	0	127
8	*Le*(Dress)	780	0.371	0.371	0.371	−0.099	−0.099	−0.099	0.470	390	0	390

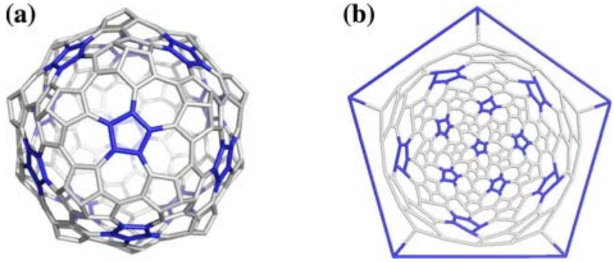


Fig. 16 Dress' cage of 260 vertices, in 3D (**a**) and Schlegel projection (**b**)

The all-pentagon capping C_5 could be important in case of the dodecahedron, since C_{20} has been identified among the products of the fullerene synthesis [17]. Thus, a cage like $C_5(E(Le(\mathrm{D})))$; $v = 180$, would be available by the self-assembling of "dodecahedron halves", fragments possible appearing in such a synthesis.

Our CageVersatile program [18] enables performing the map operations on surfaces of any genus and vertex degree lattice.

Noticeable about the cages $C_5(E(\Omega(\mathrm{D})))$ is that, in the light of simple Hückel theory, they are all open cages, excepting the leapfrog transform $C_5(E(Le(\mathrm{D})))$, which is closed (pseudo-closed shell) [19]. By leapfrogging these cages one obtains properly closed shell cages excepting $Le(C_5(E(Le(\mathrm{D}))))$, which is open shell (Table 1). For comparison, we included the cage of Dress (Fig. 16), built up on 260 atoms, and being (topological) isomer of $C_5(E(Ca(\mathrm{D})))$.

Note that the cage $C_5(E(Ca(\mathrm{D})))$; $v = 260$ was first designed by Dr. Sarah J. Austin working in the Lab. Of Prof. P. W. Fowler, Exeter University, U.K., in his Ph.D. For Cube and Tetrahedron see the figures below.

4 Kekulé structure count

The number of Kekulé valence structures of some of the above fullerenes is calculated and given in the top of the figures. For evaluating the number of Kekulé valence structures, we used the standard graph-theoretical notations. Let G be any graph with $V(G)$ and $E(G)$ being the set of its vertices and edges, respectively. For each $V_{cut} \subseteq V(G)$, $G - V_{cut}$ denotes the graph obtained from G by cutting of the vertices in V_{cut} and all edges adjacent to them. For each $E_{cut} \subseteq E(G)$, by $G - E_{cut}$ we denote the graph obtained by deleting all the edges in E_{cut}. For any (finite) set S, $|S|$ denotes the number of elements in S. Denote by $K(G)$ the set of all Kekulé structures of G.

To obtain the Kekulé structure count KSC, we used the *divide et impera* strategy. Note that, by cutting some edges, the graph disintegrates in two components. Denote the "interior" component of $G - E_{cut}$ by G_1 and "exterior" component by G_2. Let X be any subset of E_{cut}. Denote by $K = K(G)$ the set of all Kekulé (geometrical) structures of the molecule and its cardinality (i.e., KSC) as $KSC = KSC(G) = |K|$. Denote by K_X all the Kekulé structures having all the edges in X double and all edges in $E_{cut} - X$ single. Clearly, K is a disjoint union $K = \bigcup_{X \subseteq E_{cut}} K_X$, hence $|K| = \sum_{X \subseteq E_{cut}} |K_X|$. Denote $V_1(X) = \left\{v_{1,i} : e_i \in X\right\}$ and $V_2(X) = \left\{v_{2,i} : e_i \in X\right\}$. It comes out that $|K_X| = |K(G_1 - V_1(X))| \cdot |K(G_2 - V_2(X))|$ and hence:

$$KSC(G) = \sum_{X \subseteq E_{cut}} \{k(G_1 - V_1(X)) \cdot k(G_2 - V_2(X))\} \tag{18}$$

Formula (18) is the ground formula of our algorithm. It is based on the well known lemma:

Lemma 1 *Let G be any graph,* $v \in V(G)$ *and* $u_1, \ldots, u_k$ *all the neighbors of* v*. Then:*

$$KSC(G) = k(G - v - u_1) + k(G - v - u_2) + \cdots + k(G - v - u_k).$$

It is generally accepted [20] that benzenoid structures having a higher KSC would be expected to be more stable molecules. We do not use here this statement and only limit to give a way for computing this number, which is not a simple task, given being the size and tessellation of these cages.

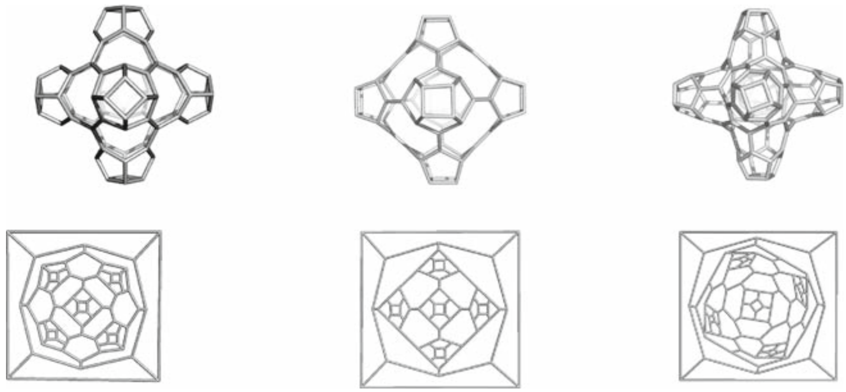
5 Conclusions

New tubercular fulleroids have been built up by using the three classical composite map operations: tripling (leapfrog *Le*), quadrupling (chamfering *Q*) and septupling (capra *Ca*) on the trivalent Platonic solids. These transforms, belonging to the tetrahedral, octahedral and icosahedral symmetry groups, show interesting mathematical properties, as shown by their covering and Kekulé structure count. It was suggested that the cage $C_5(E(Le(\mathrm{D})))$, having disjoint dodecahedron halves could be synthesized by self-assembling of these units.

Appendix

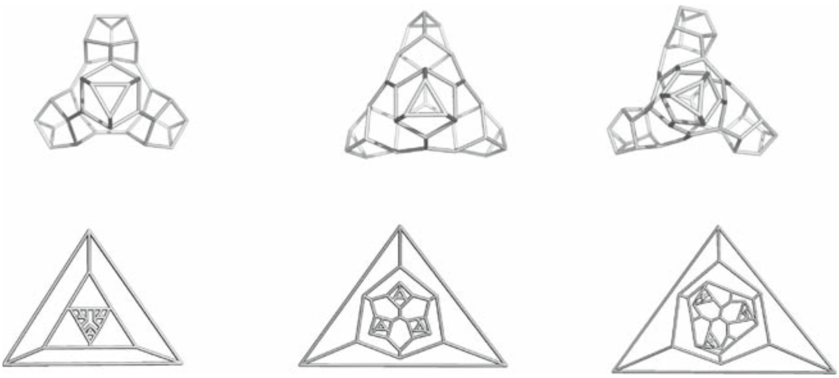
Objects derived from the Cube C and Tetrahedron T by *Le*, *Q* and *Ca* operations. The Kekulé structures count is included.

$C_5(E(Le(\mathrm{C})))$; v = 72 KSC = 57 600 | $C_5(E(Q(\mathrm{C})))$; v = 80 KSC = 18 225 | $C_5(E(Ca(\mathrm{C})))$; v = 104 KSC = 2 165 904



A1. Objects derived from the Cube C

$C_5(E(Le(\mathrm{T})))$; v = 36 KSC = 352 | $C_5(E(Q(\mathrm{T})))$; v = 40 KSC = 729 | $C_5(E(Ca(\mathrm{T})))$; v = 52 KSC = 3672



A2. Objects derived from the Tetrahedron T

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