STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LI, 1, 2006

RETRO MAP OPERATIONS

A. E. VIZITIU AND M. V. DIUDEA*

ABSTRACT. Operations on maps are well known theoretical tools for transforming a given polyhedral tessellation. Several properties of fullerenes, such as their π-electronic structure and stability, need information on their associate graph, which eventually resulted by a map operation applied on a smaller molecular graph. In this respect, retro-operations, particularly those of the most used leapfrog, chamfering and capra operations, appear particularly useful in searching the properties of fullerenes. A series of analyzed fullerenes proved to be leapfrog transforms of smaller cages. This helped in understanding their closed π-electronic structure and stability.

Introduction

Fullerenes are carbon allotropes, with finite cage associate graphs, that already entered in the realm of real chemistry: they have been functionalized or inserted in supramolecular assemblies.[1-7]

A fullerene is, according to a classical definition, an all-carbon molecule consisting entirely of pentagons (exactly 12) and hexagons (*N*/2-10). Non-classical fullerene extensions may include rings of other sizes.[8-10]

A map *M* is a combinatorial representation of a closed surface.[11] Several transformations (*i.e.*, operations) on maps are known and used for various purposes.

Operations on maps are topological-geometrical transformations enabling modification of a polyhedral tessellation. Basic simple map operations, such as dualization, truncation, stellation, etc., are supposed known. About this subject, the reader is referred to. [11-13]

Let us recall some basic relations in a map:[14]

$$\sum d\, v_d = 2e \tag{1}$$

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

In the above, v is the number of vertices, e - number of edges, f - number of faces, d - vertex degree, v_d - number of vertices of degree d and f_s - number of s-gonal faces, respectively. The two relations are joined in the famous Euler formula:[15]

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

* Faculty of Chemistry and Chemical Engineering "Babes-Bolyai" University, 400028 Cluj, Romania

with χ being the Euler *characteristic* and *g* the genus[16] 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).

This paper presents three of the most used map operations and their retro-pairs and their possible use in investigating π-electronic structure and stability of some fullerenes.

Leapfrog

Leapfrog *Le* is a composite operation,[12,17-20] which can be written as:

$$Le(M) = Du(P_3(M)) = Tr(Du(M)) \tag{4}$$

A sequence of stellation-dualization P_3-*Du* rotates the parent *s*-gonal faces by π/s. Leapfrog operation is illustrated, for a pentagonal face, in Figure 1.

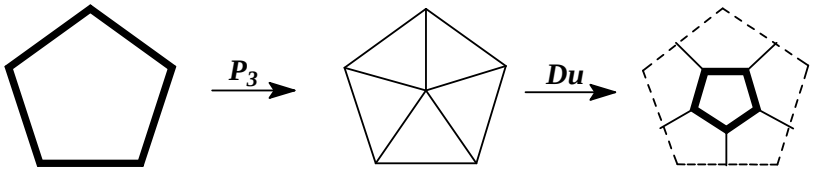

Figure 1.
Le operation on a pentagonal face

The map transformed parameters are as follows:

Le(*M*): $$v = s_0 f_0 = d_0 v_0 \; ; \; e = 3e_0 \; ; \; f = v_0 + f_0 \tag{5}$$

Retro-leapfrog *RLe* operation is based on the following sequence:

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

performed by cutting all vertices in the dual (of leapfrogged map) with degree lower than the maximal one (Figure 2). As a 3D realization, *RLe* is illustrated in Figure 3.

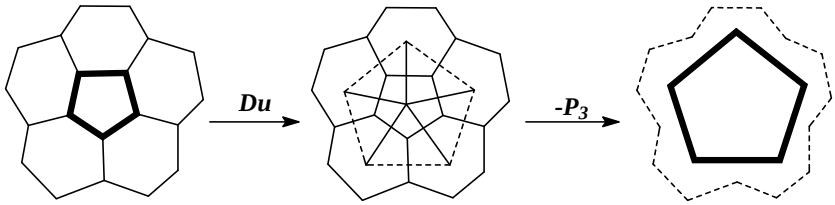

Figure 2.
Retro-Leapfrog *RLe* operation on a pentagonal face

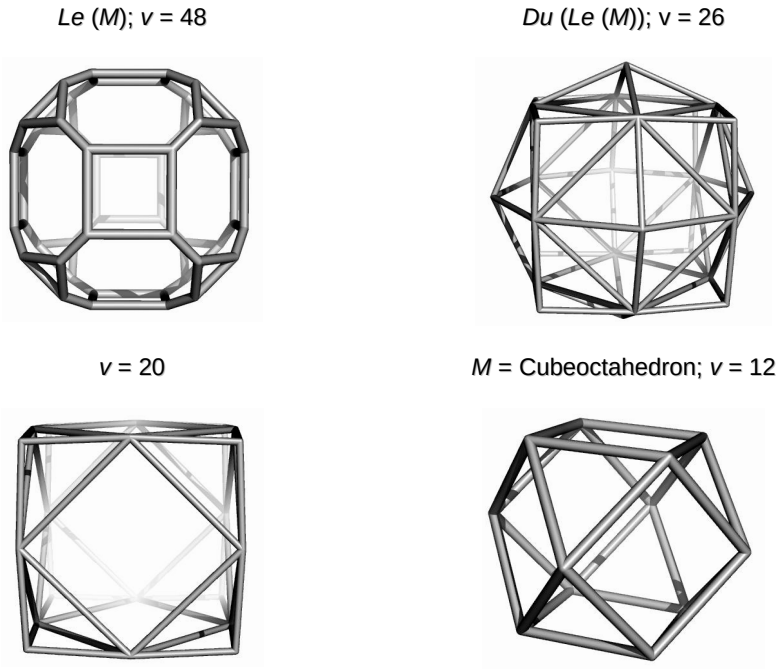

Figure 3.
Retro-Leapfrog operation

Quadrupling

Quadrupling *Q* is another composite operation, achieved by the sequence:[12]

$$Q(M) = -E(Tr_{P_3}(P_3(M))) \tag{7}$$

where *-E* means the (old) edge deletion (dashed lines, in Figure 4) of the truncation Tr_{P3} of each central vertex of P_3 capping.

The complete transformed parameters are:

$Q(M)$: $$v = (d_0 + 1)v_0;\ e = 4e_0;\ f = f_0 + e_0 \quad (8)$$

Q operation leaves unchanged the initial orientation of the polygonal faces.

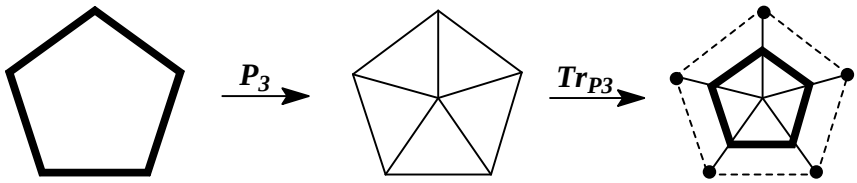

Figure 4.
Q operation on a pentagonal face

Retro-quadrupling *RQ* operation is based on the sequence:

$$RQ(M) = E(-Tr_{P_3}(P_3(M))) \quad (9)$$

performed by adding new edges parallel to the boundary edges of the parent faces (Figure 5) and deletion of these faces. As a 3D realization, *RQ* is illustrated in Figure 6.

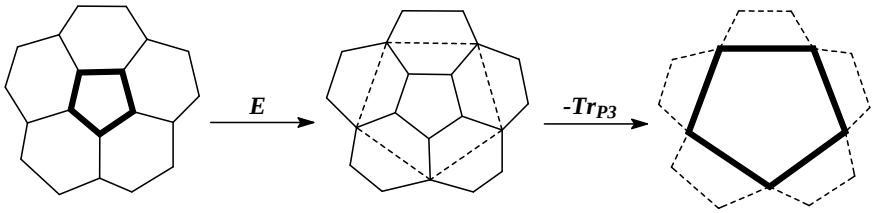

Figure 5.
Retro-Quadrupling *RQ* operation on a pentagonal face

Figure 6.
Retro-Quadrupling operation

Capra

Capra *Ca* - the goat, is the Romanian corresponding of the *leapfrog* English children game. It is a composite operation,[13,21,22] necessarily coming from the Goldberg's[23] multiplying factor *m*:

$$m = (a^2 + ab + b^2);\ a \geq b;\ a + b > 0 \qquad (10)$$

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. By this reason, *Le* is also called *tripling* and *Ca septupling*. *Q* was originally called *chamfering*.[23]

Capra is achieved by truncating the vertex located in the center of parent faces of a pentangulation P_5 transform (Figure 7). Note that, P_5 involves an E_2 (*i.e.*, edge trisection). This operation results in a map that preserves the original vertices while the parent *s*-gonal faces are twisted by π/(3/2)*s*.

The transformation can be written as:

$$Ca(M) = Tr_{P_5}(P_5(M)) \qquad (11)$$

with Tr_{P5} meaning the truncation of each vertex where P_5 capping faces of a parent face are incident. *Ca* insulates any face of *M* by its own hexagons, which are not shared with any old face (in contrast to *Le* or *Q*).

The complete transformed parameters by *Ca* are:

Ca(*M*): $$v_1 = v_0 + 2e_0 + s_0 f_0 = (2d_0 + 1)v_0;\ e_1 = 7e_0;\ f_1 = s_0 f_0 + f_0 \qquad (12)$$

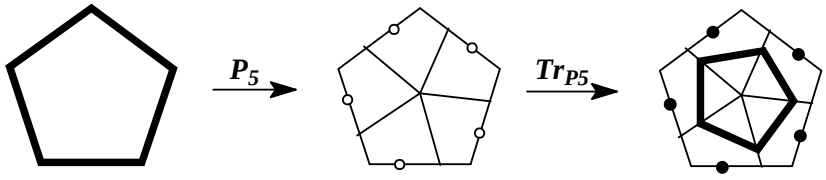

Figure 7.
Ca operation on a pentagonal face

Retro-capra *RCa* operation is achieved by the sequence:

$$RCa(M) = -E_2(-Tr_{P5}(M)) \quad (9)$$

In words, delete the smallest faces of the actual map and continue with - E_2 (Figure 8). As a 3D realization, *RCa* is illustrated in Figure 9.

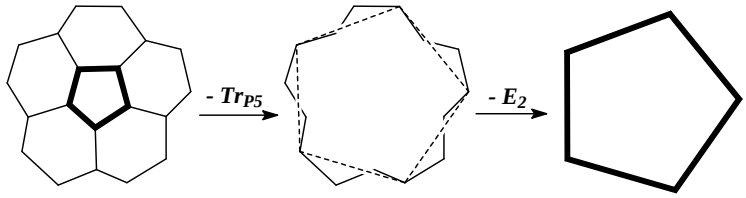

Figure 8.
Retro-Capra R*Ca* operation on a pentagonal face

C_{140} - Tr_{P_5} (D); N = 80

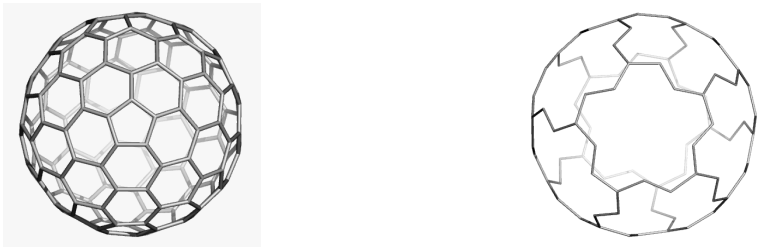

Figure 9.
Retro-Capra operation

Discussion

The properly closed PC shell *fz*-tubulenes[24] (*i.e.*, cages having fullerene halves as caps for a "zig-zag" tube) obey a true leapfrog rule, but written for zig-zag cylinders, Z-LER: $N = 13k + 3km;\ k = 4,6,8,...;\ m = 1,2,...$.

A closed structure of π-electronic shell was found[25] to be a general property of cages derived by *Le* operation from smaller objects. We just confirmed this hypothesis by drawing the parent small cages (with non-trivalent atoms corresponding to the polar rings different from hexagon) by the retro *RLe* operation (Figure 10).

The closed shell π-electronic structure of these cages is reflected in the HOMO-LUMO gap, in both simple Hűckel level of theory and PM3 calculations (Table). The heat of formation HF values of the cages with the polar ring between k = 6 and 10 are pretty low (note that the PM3 energy for C_{60} is about 13.5 kcal/mol).

Observe the Hückel gaps close in LUMO being NBO (for 0(mod(k,4) cages, Table, entries 1 and 3). Also note the cap $C_{13k/2(k\,(56)^{k/2}(665)^{k/2}-Z[3k,0])}$; k = 6, is C_{60} deducible, by taking a hexagon as the polar ring. The subscripts name is given in terms of the spiral code.[24]

The strain energy SE, in terms of POAV1 theory,[26-29] decreases as the cage size increases (Table). For comparison, SE for C_{60} is about 8.26 kcal/mol.

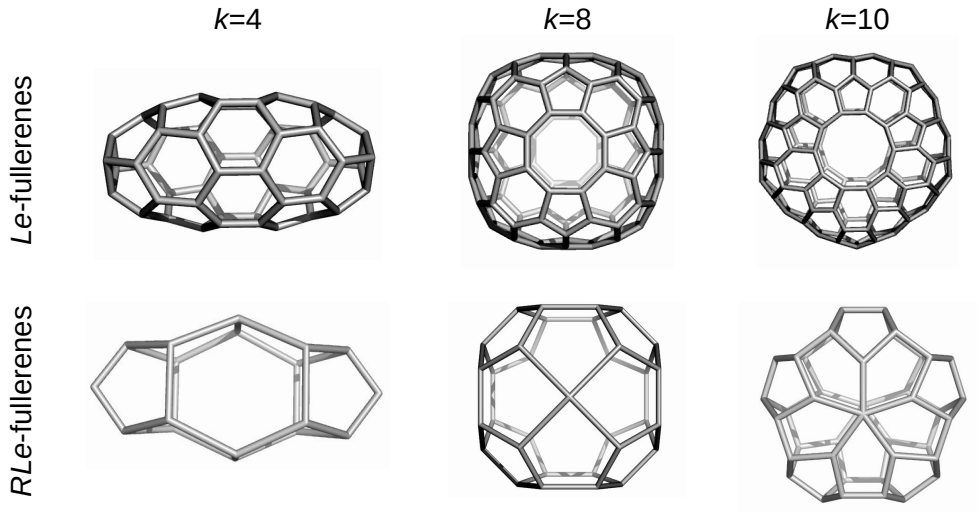

Figure 10.

*Fullerene*s of general formula $C_{N(k\,(56)^{k/2}(665)^{k/2}-Z[3k,0])}$

Table.

Data for *fz*-tubulenes $C_{N(k\,(56)^{k/2}(665)^{k/2}-Z[3k,0])}$

	Cage *k*	*v*	Sym.	PM3 HF/at. (kcal/mol)	PM3 Gap (eV)	SE POAV1 (kcal/mol)	Hűckel Data HOMO	LUMO	Gap (|β| units)	Shell
1	4	52	D_{2h}	21.585	5.533	12.526	0.256	0	0.256	PC
2	6	78	C_{3h}	12.294	6.083	6.794	0.516	-0.118	0.634	PC
3	8	104	C_{4h}	11.453	5.730	5.218	0.256	0	0.256	PC
4	10	130	C_{5h}	12.518	5.998	4.999	0.458	-0.087	0.545	PC

It is quite strange that, for the cage with *k*=8, both the heat of formation HF (Table, row 3) and strain energy SE (in POAV1 terms, Table 2, row 3, column 2) data show lower values than for the cage with *k*=6, suggesting a higher stability for the former. However, the HOMO-LUMO gap for the cage with *k*=8 is lower than for the cage with *k*=6, both at Hűckel and PM3 level of theory (Table), indicating a kinetic instability, which is supplementary supported by the non-bonding character of the LUMO orbital, in Hűckel theory.

Conclusions

Operations on maps and their retro-transformations, particularly those of the most used leapfrog, chamfering and capra operations, proved to be useful in investigating the properties of fullerenes, particularly their π-electronic structure and stability. Thus, a series of Z-LER cages proved to be leapfrog transforms of smaller cages. Among these, the cage with $k = 6$, was described as the most stable among the discussed structures, which indeed, corresponds to the isolated fullerene C_{78}.

REFERENCES

1. H. Zorc, Lj. P. Tolić, S. Martinović and D. Srzić, *Fuller*. *Sci*. *Technol*. **1994**, *2*, 471-480.
2. F. Diedrich and C. Thilgen, *Science*, **1996**, *271*, 317-323.
3. I. S. Neretin, K. A. Lyssenko, M. Yu. Antipin, Yu. L. Slovokhotov, O. V. Boltalina, P. A. Troshin, A. Yu. Lukonin, L. N. Sidorov and R. Taylor, *Angew*. *Chem*. *Int*. *Ed*. **2000**, *39*, 3273-3276.
4. W. Qian and Y. Rubin, *Angew*. *Chem*. *Int*. *Ed*. **2000**, *39*, 3133-3137.
5. K. Lee, Ch. H. Lee, H. Song, J. T. Park, H. Y. Chang and M.-G. Choi, *Angew*. *Chem*. *Int*. *Ed*. **2000**, *39*, 1801-1804.

6. T. F. Fässler, R. Hoffmann, S. Hoffmann and M. Wörle, *Angew. Chem. Int. Ed.* **2000**, *39*, 2091-2094.
7. J.-Y. Zheng, Sh. Noguchi, K. Miyauchi, M Hamada, K. Kinbara and K. Saigo, *Fullerene Sci. Technol.* **2001**, *9*, 467-475.
8. A. L. Mackay and H. Terrones, *Nature*, **1991**, *352*, 762.
9. Gao, Y. D.; Herndon, W. C. *J. Amer. Chem. Soc.* **1993**, *115*, 8459-8460
10. P. W. Fowler, T. Heine, D. E. Manolopoulos, D. Mitchell, G. Orlandini, R. Schmidt, G. Seiferth and F. Zerbetto, *J. Phys. Chem.* **1996**, *100*, 6984-6991.
11. T. Pisanski and M. Randić, in: Geometry at work: a collection of papers showing applications of Geometry (Gorini, C. A., Ed.) *Math. Assoc. Amer.*, **2000, 53**, 174-194.
12. M. V. Diudea, P. E. John, A. Graovac, M. Primorac, and T. Pisanski, *Croat. Chem. Acta*, **2003**, **76**, 153-159.
13. M. V. Diudea, *Forma* (Tokyo), **2004**, **19**, 131-163.
14. L. Euler, *Acad. Sci. I. Petropolitanae* **1736**, *8*, 128-140.
15. L. Euler, *Novi Comment. Acad. Sci. I. Petropolitanae*, **1758**, **4**, 109-160.
16. F. Harary, *Graph Theory*, Addison-Wesley, Reading, MA, **1969**.
17. V. Eberhard, Zur Morphologie der Polyeder, Leipzig,Teubner,**1891**.
18. P. W. Fowler, *Chem. Phys. Lett.* **1986**, *131*, 444-450**.**
19. P. W. Fowler and J. I. Steer, *J. Chem. Soc. Chem. Commun*. **1987**, 1403-1405.
20. J. R. Dias, *MATCH*,*Commun. Math. Comput. Chem.*, 1996, *33*, 57-85.
21. M. V. Diudea, *Studia Univ. "Babes-Bolyai"*, 2003, **48**(2), 3-16.
22. M. V. Diudea, *J. Chem. Inf. Model.,* **2005**, *45,* 1002-1009.
23. M. Goldberg, *Tôhoku Math. J.* **1937**, *43*, 104-108.
24. M. V. Diudea, *Phys. Chem., Chem. Phys.***, 2004**, *6*, 332-339.
25. P. W. Fowler and T. Pisanski, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 2865-2871.
26. R.C. Haddon, *J. Am. Chem. Soc.* **1987**, *109*, 1676-1685.
27. R.C. Haddon, *J. Am. Chem. Soc.* **1990**, *112*, 3385- 3389.
28. R.C. Haddon, *J. Am. Chem. Soc.* **1997,** *119,* 1797-1798.
29. R.C. Haddon and S.-Y. Chow, *J. Am. Chem. Soc.* **1998**, *120*, 10494-10496.