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THE "ZIG-ZAG" CYLINDER RULE

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ABSTRACT. Spectral data revealed some cluster properties of tubulenes. The "zig-zag" cylinder rule on the π-electronic structure states that properly closed shell exists in two complementary series of fullerenes derived from the 13*k* cluster, *k* = 4*m*; 4*m*+2, *m* = 1,2,…, by adding a 3*kn*, *n* =1,2,…, nanotube distancer between the two zig-zag ended caps. Semiempirical calculations support this finding.

INTRODUCTION

A fullerene is, according to a classical definition, an all-carbon molecule consisting entirely of pentagons (exactly 12) and hexagons (*N*/2-10).[1] Besides the well known near-spherical fullerenes, open ended nanotubes, capped tubules and tori have aroused both theoretical and experimental interest.[2-10] Non-classical fullerene extensions to include rings of other sizes have been considered.[11,12] Multi elemental large cages have also been studied.[13]

In simple π-only Hückel theory, the energy of the i^{th} molecular orbital $E_i = \alpha + \lambda_i \beta$ is calculated on the ground of the adjacency matrix associated to the molecular hydrogen depleted graph. Systematic studies on this matrix and their eigenvalue spectra (*i.e.*, the decreasing sequence of eigenvalues λ_i), provided some magic number rules for the stability of molecules, such as the oldest Hückel[14] 4*n* +2 rule for aromatic rings and the more recent 60 + 6*m* (*m* ≠ 1) *leapfrog* rule[15] for the properly closed fullerenes (see also ref. 16).

The π-electronic shells of neutral fullerenes are classified, function of their eigenvalue spectra, as:[17] (i) *properly closed*, PC, when $\lambda_{N/2} > 0 \geq \lambda_{N/2+1}$; (ii) *pseudo-closed*, PSC, in case $\lambda_{N/2} > \lambda_{N/2+1} > 0$; (iii) *meta-closed*, MC, with $0 \geq \lambda_{N/2} > \lambda_{N/2+1}$ and (iv) *open*, OP, when the $N/2^{th}$ (HOMO) and $N/2+1^{th}$ (LUMO) molecular orbitals are degenerate, $\lambda_{N/2} = \lambda_{N/2+1}$. The bandgap is taken as the absolute value of the difference $E_{HOMO} - E_{LUMO}$. The most frequent case is that of the pseudo-closed shell, since the number of positive eigenvalues is, in general, larger than that of the negative ones, $n_+ \geq n_-$.[18]

The other rule predicting closed-shell fullerenes is the *cylinder rule*.[19,20] Fullerenes with *k*-fold cylindrical symmetry, of general formula $C_{N,k\text{-V}[2k,n]\text{-}[6]}$, have a closed shell at each nuclearity $N = 2k(7+3m)$, m = 0, 1, 2,…, (k = 4 to 7 in this paper). These cages have a non-degenerate non-bonding orbital (NBO) LUMO separated by a gap from HOMO; in this case $n_+ = 1 + n$ -. Exceptions exist, *e.g.*, the first term of series k = 6, $C_{72,6\text{-V}[2k,1]\text{-}[6]}$, has LUMO triply degenerate, and the first term of series k = 7, $C_{84,7\text{-V}[2k,1]\text{-}[6]}$, has its NBO not the LUMO (actually is $\lambda_{N/2+3}$).

The cylinder rule, better called the "armchair" cylinder rule, can equivalently be written, in distancing tube dimension, as: $n = 1 + 3m$.

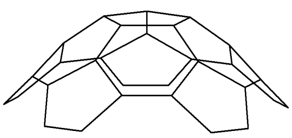
Recall that, our notations for nanotubes TUVC$_6$[*c*,*n*] and TUHC$_6$[*c*,*n*] correspond to the "armchair" (c/2, c/2) and "zig-zag" (c/2, 0), respectively.

This paper describes a further investigation of fullerenes with the aim of finding some novel rules of their electronic stability.

TUBULENES BY "ZIG-ZAG" NANOTUBE DISTANCER

A spherical fullerene, say C_{60} (I_h), can provide a cap suitable for joining an armchair nanotube (*i.e.*, a TUVC$_6$); the cap, having a *k*-fold polar ring, will be denoted by $C_{N,k\text{-V}[2k,0]}$ with N being the number of atoms in the parent fullerene. In a fullerene cluster the polar ring can vary, in our work most often k = 4, 5, 6, 7 (with the main term at k = 5). The cap $C_{N,k\text{-V}[2k,0]}$ can be used in generating a cluster of tubulenes by using a TUV distancer. The procedure is illustrated in Figure 1. This is the cluster $C_{N,k\text{-V}[2k,n]\text{-}[6]}$, obeying the armchair cylinder rule (initially defined for k = 5; 6).[19]

$C_{60,k\text{-V}[2k,0]}$; k = 5



$C_{60,k\text{-V}[2k,0]}$ + TUVC$_6$[2*k*,1]

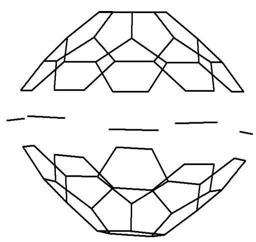
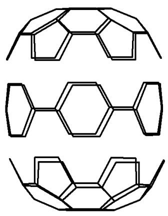


Figure 1. "Armchair" tubulene construction

$C_{72,k\text{-V}[2k,0]}$ + TUVC_6[2k,3]; k = 6



C_{18k}

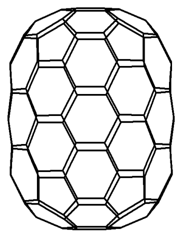
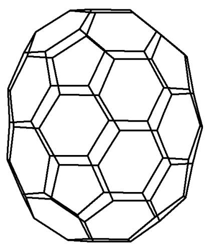


Figure 1. (continued)

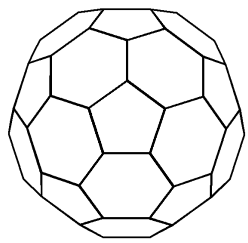
The first term of the sub-cluster $C_{60,5\text{-V}[10,1]\text{-}[6]}$ is just the isolated fullerene C_{70} (see below). Its topology is given as the spiral code.[21,22] We amended this code by specifications for the mode of inserting the new polygon, either by an edge (*e*) or by an angle (*a*).

$C_{60,5\text{-V}[10,1]\text{-}[6]} = C_{70}$



k, 6*k*, (*a*5, *e*6)*k*, (*e*6, *e*6)*k*, (*a*5, *e*6)*k*, *k*
k = 4; 5; 6; 7

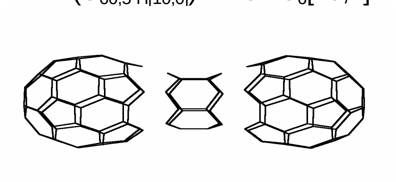
C_{70}; (top)



Cluster $C_{14k;}$ k = 4; 5; 6; 7
N =14k; 56; 70; 84; 98

A different cap, denoted $C_{N,k\text{-H}[2k,0]}$, is that favoring the coupling with a zig-zag nanotube (*i.e.*, TUHC_6).[20] Figure 2 gives such an example.

2($C_{60,5\text{-H}[10,0]}$) + TUHC_6[10,2]



$C_{60,5\text{-H}[10,3]\text{-}[7,6,7]}$

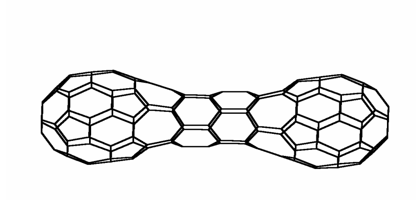


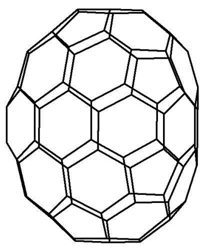
Figure 2. "Zig-zag" tubulene construction

A tubulene $C_{N,k\text{-V}[2k,6]\text{-}[6]}$ can be viewed as originating in the coalescence product of two spherical fullerenes, namely the $C_{N,k\text{-H}[2k,1]\text{-}[7]}$, from which it results by a series of Stone-Wales[23,24] edge flipping. Similar coalescence reactions between spherical cages and nanotubes have been considered.[25]

Resuming to the nomenclature, the *C* letter (*i.e.*, cage) is followed by the number of atoms *N* of the parent fullerene, having a *k*-fold polar ring, the cap being attached to a V/H[*c*,*n*] tube (with a cross-section of *c* atoms, and *n* atom rows distancing the two caps; *n* = 0 for the cap, only). The numbers in the last brackets denote the tiling polygons in the region between the two caps.

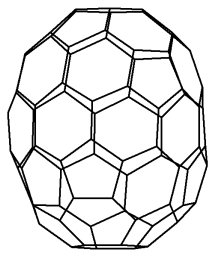
A quite different cap $C_{N,k\text{-H}[c,0]}$ is provided by the isolated fullerene C_{78}, the two of its IP (*i.e.*, isolated pentagon) isomers being given below.

$C_{78}a$; C_S



k, (5, 6)*k*/2, (*a*6, *a*6, *e*5)*k*/2, (*a*6)*k*, (*e*5, *a*6, *a*6)*k*/2, (6, 5)*k*/2, *k*
k = 6

$C_{78}c$; C_1

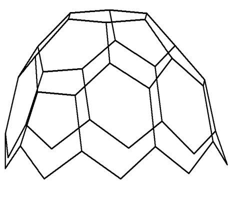


Cluster C_{13k}; *k* = 4; 6; 8; 10

N =13*k*; 52; 78; 104; 130

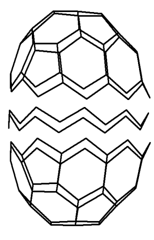
The formal building of the related tubulenes is illustrated in Figure 3.

$C_{78,k\text{-H}[3k,0]}$; *k* = 6



$C_{78,k\text{-H}[3k,0]}$ + TUHC$_6$[3*k*,2]

$C_{78,k\text{-H}[3k,0]}$ + TUHC$_6$[3*k*,1]



$C_{78,k\text{-H}[3k,2]\text{-}[6]} = C_{19k}$; *k* = 6

Figure 3. "Zig-zag" tubulenes derived from C_{78}

SPECTRAL PROPERTIES OF THE NOVEL CLUSTER

The zig-zag tubulenes derived from the cluster C_{13k} form a properly closed shell tubulene cluster with the general formula $C_{13k,k\text{-}H[3k,n]\text{-}[6]}$ and the following construction $N = 13k + 3kn;\ k = 4m + 2z;\ m = 1,2,...;\ z = 0,1;\ n = 1,2,...$. It shows the same bandgap for a given z value at each positive n. The last parameter is just the n-dimension of the distancing tube and it discriminates between the twin odd and even sub-clusters (see Figures 4 and 5).

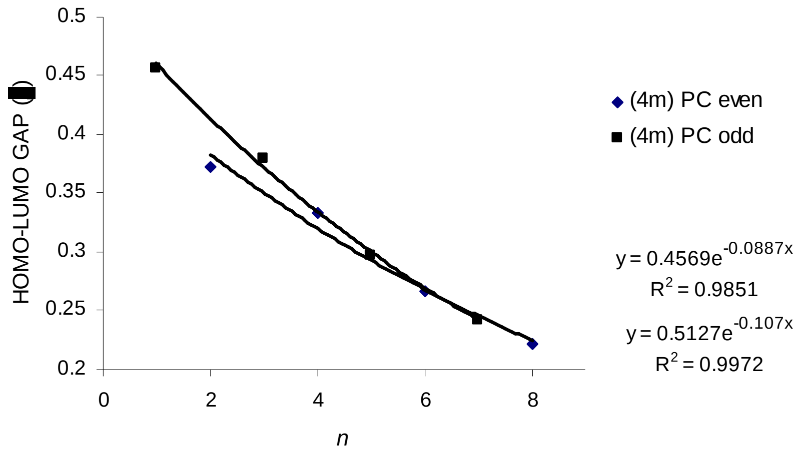


Figure 4. The plot of the spectral gap vs. n, in the series $k = 4m$

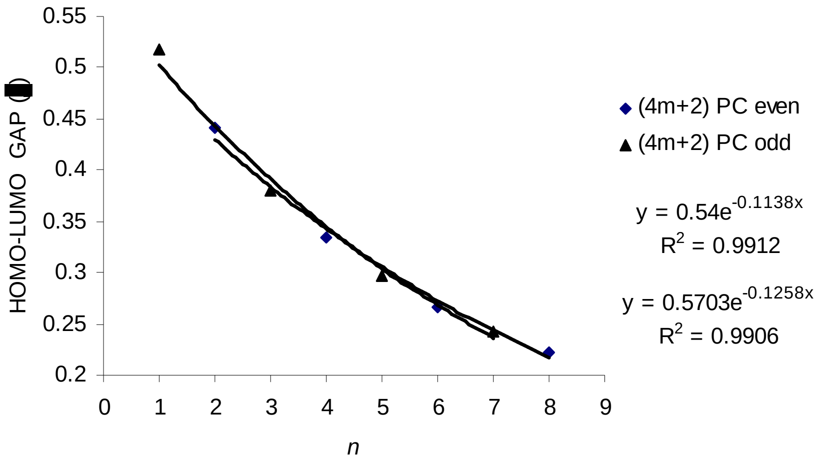


Figure 5. The plot of the spectral gap vs. *n*, in the series $k = 4m+2$

In the opposite to the 1st (armchair) cylinder rule, the terms for $n = 0$ do not (properly) belong to the new cluster. In the series $k = 4m$, LUMO is an NBO (not encountered at higher *n*-values) while in the series $k = 4m+2$, the gaps are different for different *m*-values. The identity of the gaps appears only at $n > 0$. Figure 6 gives the repeating units of the twin sub-clusters, in the so-called geodesic projection.

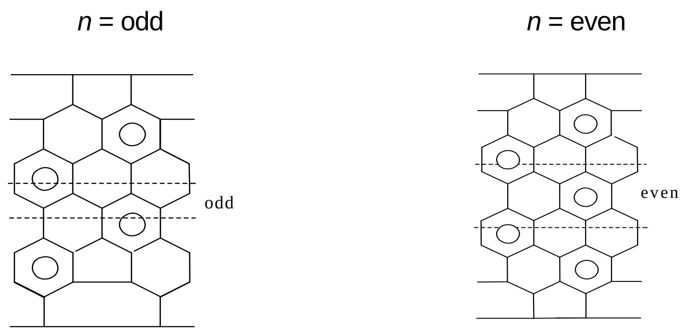


Figure 6. Geodesic projection of the repeating units of the twin sub-clusters with the general formula $C_{13k,k\text{-H}[3k,n]\text{-}[6]}$

The novel cluster $C_{13k,k\text{-H}[3k,n]\text{-}[6]}$, of properly closed shell fullerenes, having $N = 13k + 3kn;\ n = 1,2,...$ and equal number of positive and negative eigenvalues $n_+ = n_-$, we call *the zig-zag cylinder rule*, to specify the type of the tube distancing the two caps. This cluster does nos superimposes over the leapfrog[15,18,19] (properly closed-shell) fullerenes with the exception of the cages having $k = 6$. The spectral data are supported by semiempirical calculations (see Table 1).

In going from one sub-cluster to the other, complementary (twisted) series of pseudo-closed shell tubulenes appear. Figure 7 shows the plots of PSC and PC series corresponding to $k = 6$ (viewed as single odd&even series). Clearly, the gap is deeper for the PC series, suggesting a higher kinetic stability of the corresponding tubulenes. Note that the term $n = 0$ in PSC is just the C_{78}c; C_1 (see above).

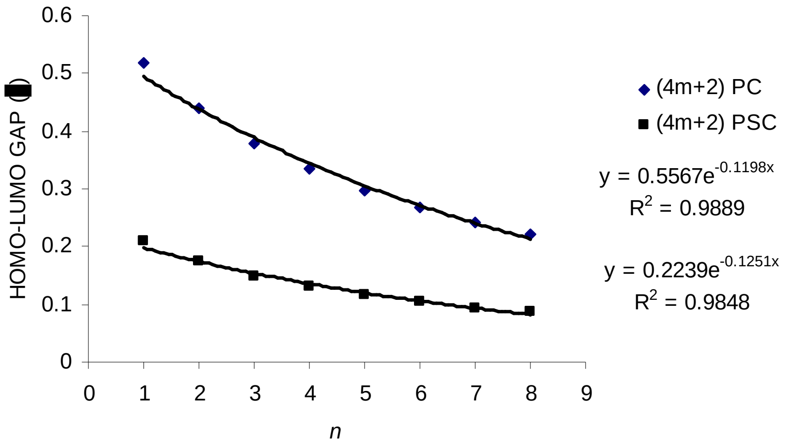


Figure 7. Comparison between the PSC and PC series corresponding to $k = 6$

In the case of objects with formula $C_{N,k\text{-H}[2k,n]\text{-}[7,6,7]}$ (see Figure 2) the open shell appears, starting with the first row of hexes ($n = 2$) distancing the two caps. The two frontier orbitals degenerate within the positive domain of eigenvalue for $k = 4$, while for higher k they are located either in the positive or negative domain (as in some tetrahedral fullerenes, with $N \geq 628$).[18] The most important exception is $C_{72,6\text{-H}[12,2]\text{-}[7,6,7]}$ ($N = 156$), with a meta-closed shell. The "accidental" gap is, however, very thin (-0.026439; -0.028345). This is the only case of MC shell reported in spherical fullerenes (more exactly, fullerenes of genus zero).[18]

SEMIEMPIRICAL CALCULATIONS

The semiempirical calculations were calculated with the PM3 Hamiltonian (by HyperChem software package).[26] Data are given in Table 1.

Fowler[27] has found that geometric instability appears in fullerenes at a "small" gap of *ca*. 5 eV, in semiempirical calculation, or 0.4 |β| in simple Hückel calculation. At least the first terms, and particularly in the series $k = 4m+2$

(Table 1, entries 4-6 and 10-12), show favorable bandgap and relatively low heat of formation (per atom). Compare these data with those for C_{60}: HF = 13.512; PM3 Gap = 6.594 and find that we are in the same domain. Besides the isolated C_{78} (entry 4), some other tubulenes can be candidates to the status of real molecules. A cage having a 10-fold face could appear strange but it just obeys the Hückel 4*m*+2 aromatic rule.

Table 1.

Data for the tubulenes $C_{13k,k\text{-H}[3k,n]\text{-}[6]}$

	Cage *k*; *n*	*N*	Sym.	PM3 HF/at. (kcal/mol)	PM3 GAP (eV)	Spectral Data $\lambda_{N/2}$	$\lambda_{N/2+1}$	GAP (|β| units)	Shell
1	4; 0	52	D_{2h}	21.585	5.533	0.2564	0	0.2564	PC
2	4; 1	64	S_4	19.271	5.783	0.3789	-0.0774	0.4563	PC
3	4; 2	76	D_{2h}	18.162	5.469	0.3260	-0.0470	0.3731	PC
4	**6; 0**	**78**	$\boldsymbol{C_s}$	**12.294**	**6.083**	**0.5157**	**-0.1176**	**0.6333**	**PC**
5	6; 1	96	D_{3d}	11.015	5.564	0.4329	-0.0844	0.5173	PC
6	6;2	114	$\boldsymbol{C_s}$	10.381	5.195	0.3688	-0.0721	0.4409	PC
7	**8; 0**	**104**	$\boldsymbol{C_{4h}}$	**11.453**	**5.730**	**0.2564**	**0**	**0.2564**	**PC**
8	8; 1	128	D_{4d}	10.158	5.497	0.3789	-0.0774	0.4563	PC
9	8; 2	152	C_{4h}	9.390	5.112	0.3260	-0.0470	0.3731	PC
10	**10; 0**	**130**	$\boldsymbol{C_{5h}}$	**12.518**	**5.998**	**0.4579**	**-0.0874**	**0.5453**	**PC**
11	10; 1	160	D_{5d}	11.875	5.512	0.4329	-0.0844	0.5173	PC
12	10; 2	190	C_{5h}	10.715	5.115	0.3688	-0.0721	0.4409	PC

CONCLUSIONS

The zig-zag cylinder rule, first reported in this paper, presents a cluster with the general formula $C_{13k,k\text{-H}[3k,n]\text{-}[6]}$, of properly closed shell tubulenes, having $N = 13k + 3kn;\ n = 1,2,...$ .The number *n* is just the number of atom rows in the tube distancing the two caps. It shows the same bandgap for either odd or even *k* value at each positive *n*. The semiempirical calculations support the idea of relatively stable molecules, possible appearing in the soot of the vaporized graphite.

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