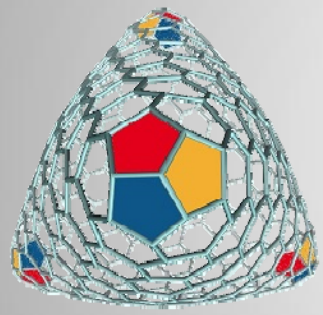
WEST UNIVERSITY OF TIMIȘOARA
FACULTY OF CHEMISTRY, BIOLOGY, GEOGRAPHY
DEPARTMENT OF BIOLOGY-CHEMISTRY
LAB. OF STRUCTURAL AND COMPUTATIONAL PHYSICAL-CHEMISTRY FOR NANOSCIENCES & QSAR (CFSCNQ)
Prof. dr. dr. habil. Mihai V. PUTZ
Director CFSCNQ
mv_putz@yahoo.com

CHEMICAL GRAPH THEORY

- Pictorial Introduction Part 2



Dr. Ottorino ORI
Actinium Chemical Research
Rome
ottorino.ori@gmail.com

TOPOLOGICAL MODELING (TM)

- Chemical systems simulated by the *minimization of distance based invariants*, namely the **Wiener index** *W* ***and the*** *topological efficiency index ρ or sphericithy index (see previous talk).*

- *We call this elegant computational approach Topological Modeling (TM).*

See: **Wiener Index Role in Topological Modeling of Hexagonal Systems – From Fullerenes to Graphene**, Ali Iranmanesh, Ali Reza Ashrafi, Ante Graovac,Franco Cataldo, Ottorino Ori MCM13, I. Gutman, B. Furtula (Eds.), Distance in Molecular Graphs – Applications, Univ. Kragujevac, Kragujevac, 2012, pp.135–155 AND RELATED REFERENCES

TOPOLOGICAL MODELING (TM)

- *Topological Modeling (TM)* relies on the **strong approximation** that **similar carbon** systems tendto arrange their structures minimizing the graph invariant *W* seen like **the inteartomic, long-range potential connecting all pairs of carbon atoms**.

- *This potential is proportional to d^1, whereas harmonic potential is proportional to d^2*

TOPOLOGICAL MODELING (TM)

- Some inspirations help heuristically.

- One of the best example consists in C_{60} fullerene which has 1812 non-isomorphic isomers, and the *physically stable isomer with icosahedral symmetry and only* isolated pentagons corresponds to the isomer *with the minimum W value W=8340.*

TOPOLOGICAL MODELING (TM)

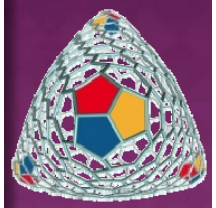
- Then we may sieve good candidates among the molecules with low Wiener, which are topologically the most compact in a set of isomers.

W index minimum principle for similar structures:

SYSTEM COMPACTNESS → *CHEMICAL STABILITY*

On the other side *SYSTEM COMPACTNESS* → *W MINIMIZATION*

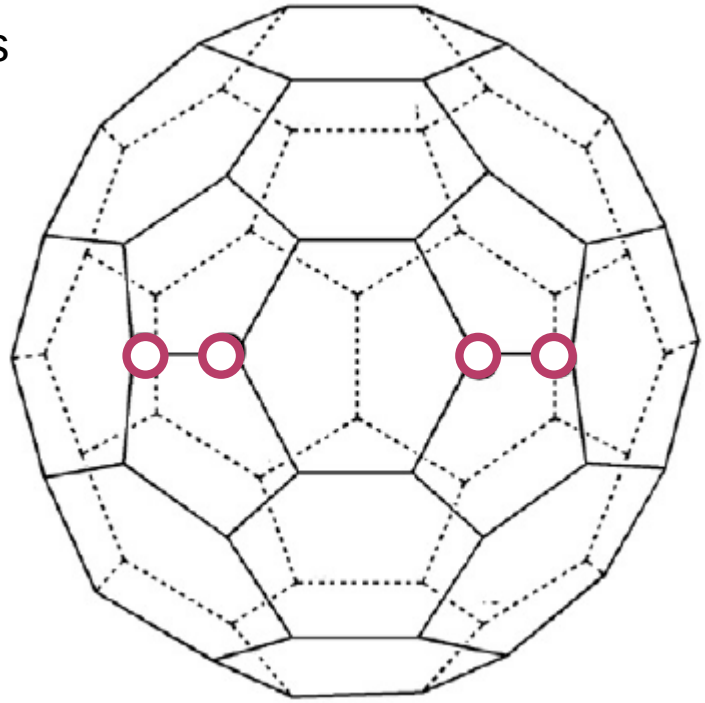
then *W MINIMIZATION* → *CHEMICAL STABILITY*



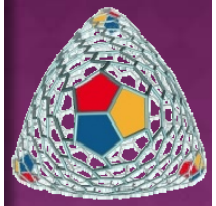
TOPOLOGICAL MODELING (TM)

- **The successful case of C_{66} fullerene**

(n/2–10) hexagons
and 12 pentagons



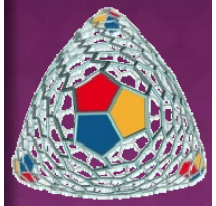
C_{66}–2v stable isomer in $Sc_2@C_{66}$
metallofullerene



TOPOLOGICAL MODELING (TM)

- **The successful case of C_{66} fullerene**

Group theoretical studies assign to the C_{66} fullerene 4478 distinct non-IPR cages, grouped in six distinct families $2xD_3$, $1xC_{3v}$, $18xC_{2v}$, $112xC_s$, $211xC_2$, $4134xC_1$ In this large isomeric space, the search for possible stable molecules get greatly simplified by the high resolution ^{13}C NMR spectrum (19-lines with multiplicity 5x2; 14x4) that reduces just to 18 candidates with C_{2v} symmetry the choice for the C_{66} cage entering in the experimentally produced $Sc_2@C_{66}$ cluster The hunt for the most stable cage is then reduced to 18 molecules.



TOPOLOGICAL MODELING (TM)

- **The successful case of C_{66} fullerene**

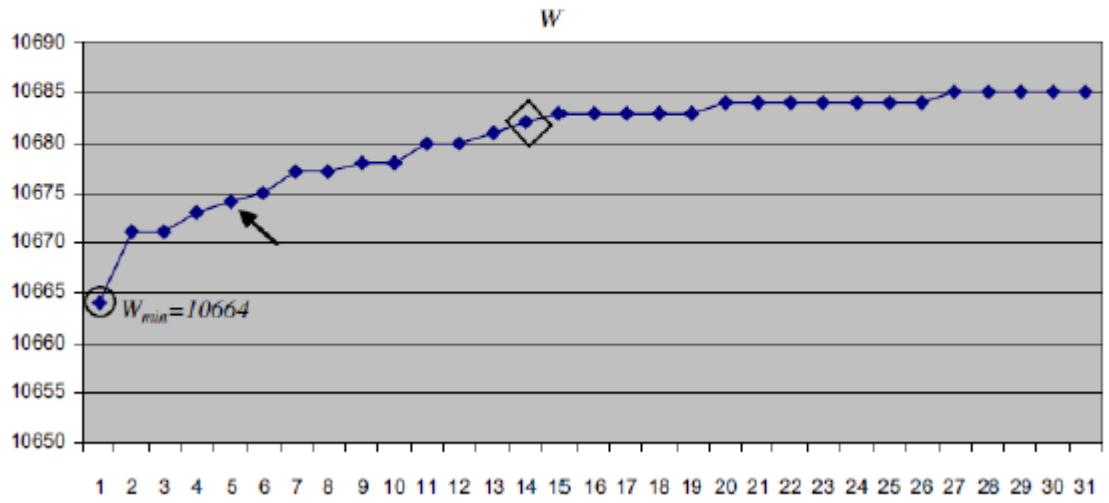
Connectivity information stored in the C_{66}-$C_{2v}^{\#0011}$ molecular graph.

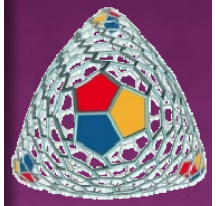
Face	Ring	Connected faces	Molecular graph nodes
1	5	2 14 21 31 35	1 2 3 4 5
2	5	1 13 21 33 35	3 4 6 7 8
3	5	4 14 22 32 35	9 10 11 12 13
4	5	3 13 22 34 35	11 12 14 15 16
5	5	16 25 29 30 33	17 18 19 20 21
6	5	18 26 29 30 34	22 23 24 25 26
7	5	15 23 27 28 31	27 28 29 30 31
8	5	17 24 27 28 32	32 33 34 35 36
9	5	15 16 19 23 25	37 38 39 40 41
10	5	17 18 20 24 26	42 43 44 45 46
11	5	19 20 23 24 27	47 48 49 50 51
12	5	19 20 25 26 30	52 53 54 55 56
13	6	2 4 29 33 34 35	6 7 15 16 57 58
14	6	1 3 28 31 32 35	1 2 9 13 59 60
15	6	7 9 16 21 23 31	29 30 37 41 61 62
16	6	5 9 15 21 25 33	17 21 40 41 63 62
17	6	8 10 18 22 24 32	34 35 43 44 65 66
18	6	6 10 17 22 26 34	22 23 44 45 64 65
19	6	9 20 12 11 23 25	38 39 49 50 52 56
20	6	10 11 12 19 24 26	49 52 48 42 46 53
21	6	1 2 15 16 31 33	4 5 8 63 61 62
22	6	3 4 17 18 32 34	10 11 14 64 65 66
23	6	7 9 11 15 19 27	30 31 37 38 50 51
24	6	8 10 11 17 20 27	35 36 42 43 48 47
25	6	5 9 12 16 19 30	17 18 39 40 55 56
26	6	6 10 12 18 20 30	26 22 53 54 45 46
27	6	7 8 11 23 24 28	27 32 36 47 31 51
28	6	7 8 14 27 31 32	27 28 32 33 59 60
29	6	5 6 13 30 33 34	19 20 24 25 57 58
30	6	5 6 12 25 26 29	19 25 18 55 26 54
31	6	1 7 14 15 21 28	1 5 28 60 29 61
32	6	3 8 14 17 22 28	9 10 33 59 34 66
33	6	2 5 13 16 21 29	7 8 20 58 21 63
34	6	4 6 13 18 22 29	14 15 24 57 23 64
35	6	1 2 3 4 13 14	2 13 12 16 3 6

TOPOLOGICAL MODELING (TM)

- **The successful case of C_{66} fullerene**

Figure 2 The ab initio most stable isomers are *all* located near the W_{min}=10664 point: C_{66}–$C_s^{\#0060}$ (circled corresponds to W_{min}); C_{66}-$C_{2v}^{\#0011}$ (arrowed, W=10674); C_{66}-$C_2^{\#0083}$ (diamond, W=10682).

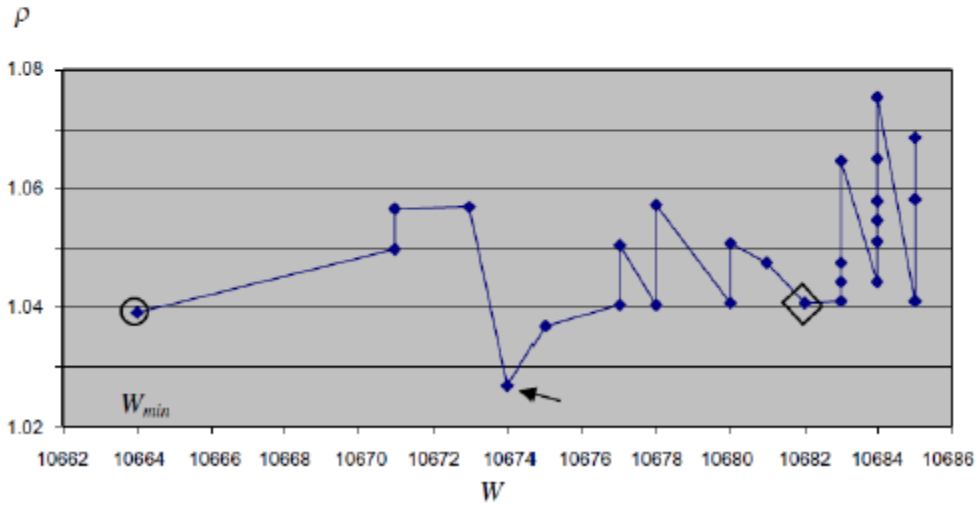


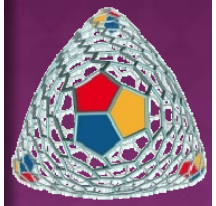


TOPOLOGICAL MODELING (TM)

- **The successful case of C_{66} fullerene**

Figure 3 Scattered values (W, ρ) for the 31 most stable C_{66} isomers. C_{66}–$C_s^{\#0060}$ (circled corresponds to ρ= 1.0391); C_{66}-$C_{2v}^{\#0011}$ (arrowed, ρ= 1.0268); C_{66}-$C_2^{\#0083}$ (diamond, ρ= 1.0408). Experimentally stable fullerene C_{66}-$C_{2v}^{\#0011}$ emerges as a local mimimun in our simulations.



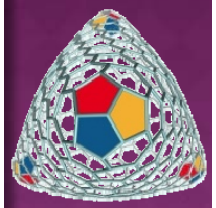


TOPOLOGICAL MODELING (TM)

- We may resume our results in a rule:

→ *In the (W, ρ) plane, stable isomers of a given chemical systems are located in the local minima of the ρ(W) scattered curve.*

- Future investigation, expecially from Students, are most than welcome !!



DISTANCE BASED GRAPH INVARIANTS IN INFINITE SYSTEMS

- A very nice computational feature of distance based graph invariants is their polynomial-like behavior. This peculiar character has been evidence by Bonchev and Mekenyan cubic formula for W(N) valid for all POLYMERS

  D. Bonchev, O. Mekenyan, A Topological Approach to the Calculation of the π- electron Energy and Energy Gap of Infinite Conjugated Polymers, Z. Naturforsch.,35a (1980) 739-747.

$$W(N) = a_3 N^3 + a_2 N^2 + a_1 N + a_0,$$

$$\underline{k} = 3 \quad \text{for} \, d_T = 1 \, \text{lattices}.$$

DISTANCE BASED GRAPH INVARIANTS IN INFINITE SYSTEMS

- Some simple examples:

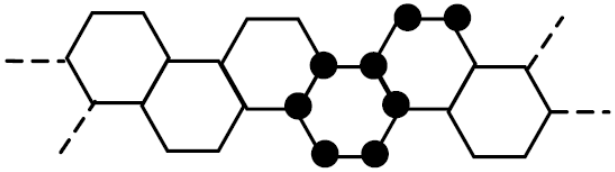
see also Cataldo, Franco , Ori, Ottorino andIglesias-Groth, Susana (2010) 'Topological lattice descriptors of graphene sheets with fullerene-like nanostructures', Molecular Simulation, 36: 5, 341 – 353.

(a)

$$W(N)_{\mathrm{LIN}} = \frac{(N^3 - N)}{6},$$

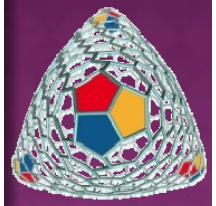
$$W(N)_{\mathrm{ZZ}} = \frac{N^3 + 50N - 144}{12}.$$

(b)



$$W(N)^{\mathrm{C}}_{\mathrm{LIN}} = \frac{N^3 - N}{8},$$

$$W(N)^{\mathrm{C}}_{\mathrm{ZZ}} = \frac{N^3 + 64N}{16}.$$



DISTANCE BASED GRAPH INVARIANTS IN INFINITE SYSTEMS

- GENERAL SOLUTION - conjectured:

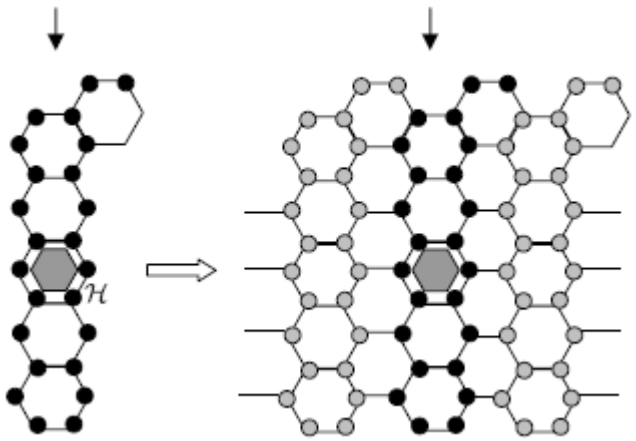
$$W(N) = a_{\underline{k}} N^{\underline{k}} + a_{\underline{k}-1} N^{\underline{k}-1} + \cdots + a_1 N + a_0,$$

$$\text{with } \underline{k} = (2d_T + 1)/d_T.$$

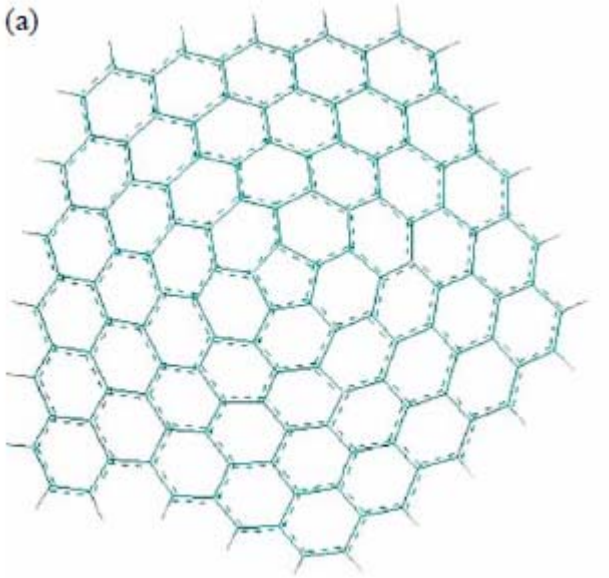
APPLICATION TO INFINITE GRAPHENE-LIKE SYSTEMS

- We compare now a graphene ribbon and a nanocone (**a portion of ….. ?**).

ZZ5 graphene



NANOCONE



APPLICATION TO INFINITE GRAPHENE-LIKE SYSTEMS

- ZZ5 graphene The same invariants in the dual lattice ZZ_5^D assume the expressions:

$$W^D(N) = N^3/30 + 115N/6 - 188$$

$$M^D(N) = N/5 - 1$$

$$\underline{w}^D = N^2/20 + 20$$

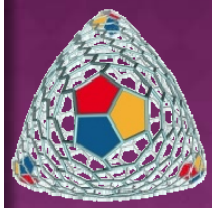
- NANOCONE F^D (**a portion of ?**

$$N = 1 + 5/2\,(f^2 + f) \qquad f \geq 0$$

and the distance-based invariants for dual nanocone F^D:

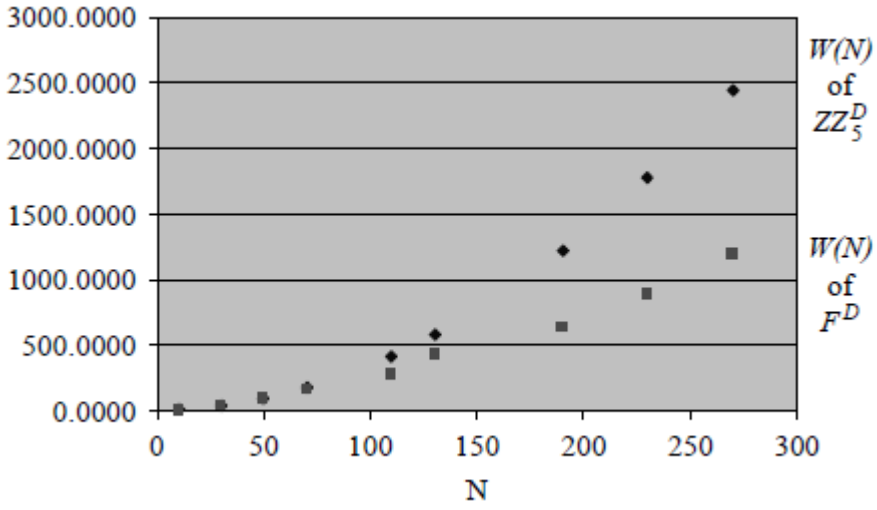
$$W^D(f) = (62f^5 + 155f^4 + 160f^3 + 85f^2 + 18f)/24$$

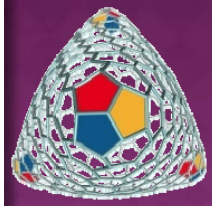
$$M^D(f) = 2f$$



APPLICATION TO INFINITE GRAPHENE-LIKE SYSTEMS

Topological modeling predicts that, for any size N of the relative (dual) graphs, the fullerene-like structure FD shows a higher compactness (hence a higher chemical stability) of the reference graphenic layers.





APPLICATION TO INFINITE GRAPHENE-LIKE SYSTEMS

- SOME MORE TERRIFIC MAGICS

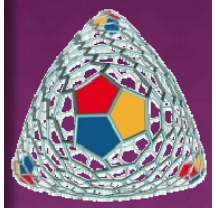
WARNING for Math addicts only

$$s = k/d_T = 2 + 1/d_T$$

May be inverted to derive the new
WIENER – based **DIMENSIONALITY**

$$d_W = (s-2)^{-1}$$

Bridges lattice topological compactness,
expressed by topological invariant $W(N) \approx N^s$
the lattice dimensionality



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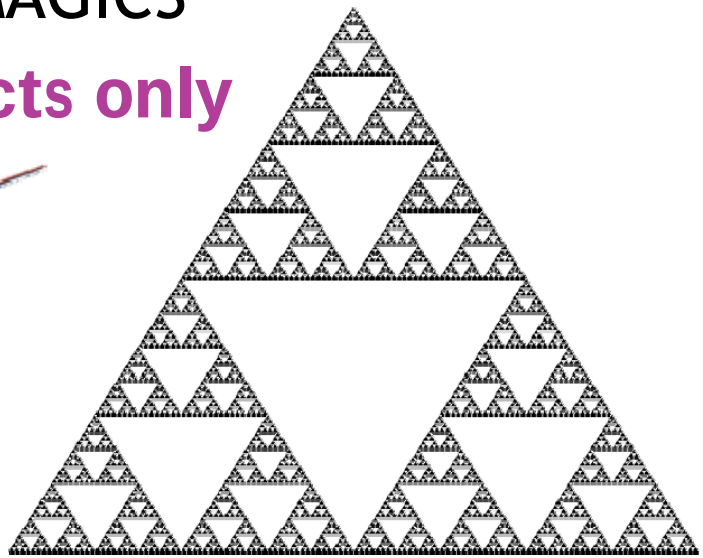


$$\lim_{N\to\infty} \ln_N W(N) = 2 + \frac{\ln 2}{\ln 3}$$ for $d_T = 2$ Sierpinski gasket

$$\lim_{N\to\infty} \ln_N W(N) = 2 + \frac{\ln 3}{\ln 8}$$ for $d_T = 2$ Sierpinski carpet

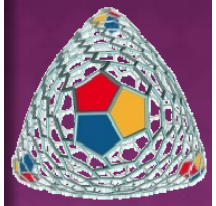
APPLICATION TO INFINITE GRAPHENE-LIKE SYSTEMS

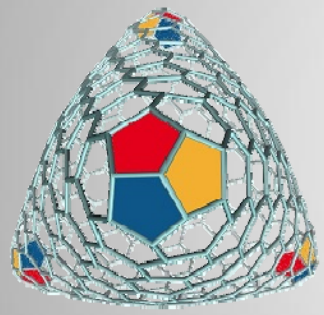
- SOME MORE TERRIFIC MAGICS

WARNING for Math addicts only

$$\lim_{N\to\infty} \ln_N \frac{W(N)}{N^2} = d_W^{-1}$$

generally applicable to any d_T-dimensional infinite graphs.





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MANY THANKS FOR YOUR ATTENTION

Questions ?

Ottorino ORI

Actinium Chemical Research

Rome

ottorino.ori@gmail.com