STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, 4, 2009

CORSU NETWORK - A NEW GRAPHENE DESIGN

MIRCEA V. DIUDEA[a] AND ALEKSANDAR ILIĆ[b]

ABSTRACT. A new graphene pattern, called CorSu, was designed and the energy of some small fragments of the lattice, functionalized by groups containing oxygen, carbon, nitrogen and phosphorus, was evaluated at the level of semiempirical method PM3. The topology of the network is described in terms of Omega counting polynomial. Close formulas for calculating the polynomial and the Cluj-Ilmenau index derived from this polynomial are given.

Keywords: Counting polynomial, lattice, CI index.

INTRODUCTION

Nano-era can be the name of the last twenty years, period when several new carbon allotropes have been discovered and studied for applications in nano-technology, in view of reducing the dimensions of devices and increasing their performance, al a lower cost of energy and money. Among the carbons structures, fullerenes (zero-dimensional), nanotubes (one dimensional), graphene (two dimensional) and spongy carbon (three dimensional) represent the novelty [1,2]. The attention of scientists was also focused to inorganic compounds, a realm where almost any metal atom can form clusters, tubules or crystal networks, very ordered structures at the nano-level. Recent articles in crystallography promoted the idea of topological description and classification of crystal structures [3-8]. They present data on real, but also hypothetical lattices, designed by computer.

The present study deals with a hypothetical graphene patterned by coronene- and sumanene-like units, described in terms of Omega counting polynomial and evaluated as energy by the PM3 method.

OMEGA POLYNOMIAL

Let $G(V,E)$ be a connected graph, with the vertex set $V(G)$ and edge set $E(G)$. Two edges $e = uv$ and $f = xy$ of G are called *codistant e co f* if they obey the following relation [9]:

[a] *Faculty of Chemistry and Chemical Engineering, "Babes-Bolyai" University, 400028 Cluj, Romania, diudea@gmail.com*

[b] *Faculty of Sciences and Mathematics, University of Niš, Višegradska 33, 18000 Niš, Serbia, aleksandari@gmail.com*

$$d(v,x) = d(v,y) + 1 = d(u,x) + 1 = d(u,y) \quad (1)$$

Relation *co* is reflexive, that is, *e co e* holds for any edge *e* of *G*; it is also symmetric, if *e co f* then *f co e*. In general, relation *co* is not transitive; an example showing this fact is the complete bipartite graph $K_{2,n}$. If "*co*" is also transitive, thus an equivalence relation, then *G* is called a *co-graph* and the set of edges $C(e) := \{f \in E(G);\ f\ co\ e\}$ is called an *orthogonal cut oc* of *G*, *E*(*G*) being the union of disjoint orthogonal cuts:

$$E(G) = C_1 \cup C_2 \cup ... \cup C_k,\ C_i \cap C_j = \varnothing, i \neq j\ .$$

Klavžar [10] has shown that relation *co* is a theta Djoković-Winkler relation [11,12].

We say that edges *e* and *f* of a plane graph *G* are in relation *opposite, e op f,* if they are opposite edges of an inner face of *G*. Note that the relation *co* is defined in the whole graph while *op* is defined only in faces. Using the relation *op* we can partition the edge set of *G* into *opposite* edge *strips, ops.* An *ops* is a quasi-orthogonal cut *qoc*, since *ops* is not transitive.

Let *G* be a connected graph and S_1, S_2, ..., S_k be the *ops* strips of *G*. Then the *ops* strips form a partition of *E(G)*. The length of *ops* is taken as maximum. It depends on the size of the maximum fold face/ring F_{max}/R_{max} considered, so that any result on Omega polynomial will have this specification.

Denote by *m*(*G*,*s*) the number of *ops* of length *s* and define the Omega polynomial as [13-15]:

$$\Omega(G,x) = \sum_s m(G,s) \cdot x^s \quad (2)$$

Its first derivative (in *x*=1) equals the number of edges in the graph:

$$\Omega'(G,1) = \sum_s m(G,s) \cdot s = e = |E(G)| \quad (3)$$

On Omega polynomial, the Cluj-Ilmenau [9] index, *CI*=*CI*(*G*), was defined:

$$CI(G) = \{[\Omega'(G,1)]^2 - [\Omega'(G,1) + \Omega''(G,1)]\} \quad (4)$$

Within this paper, the main results refer to F_{max}(6). If rings instead of faces are considered, the polynomial is different. The inclusion of hexagons lying "under" the bridge brings complications in the number and length of *ops*, particularly at the maximum length.

Data were calculated by an original program called Nano Studio [16], developed at the TOPO Group Cluj.

LATTICE BUILDING

The lattice was built on the graphene sheet, of (6,3) tessellation, by decorating it with coronene-like flowers, having sumanene units as petals. The pattern, called CorSu, can be described as: [6:(6:(5,6)3)6], with vertices/atoms of degree 3 (sp^2) and 4 (sp^3), as shown in Figure 1.

This idea came out from the TOPO Group Cluj older studies on aromaticity, in which circulene/flower units were proposed as extensions of the Clar theory of aromaticity. Notice, the coronene and sumanene are molecules synthesized in the labs. It was also supported by the synthesis of several bowl-shaped molecules, inspired from the architecture of fullerenes and, more recently, by the direct synthesis of fullerenes starting from open precursors. The design of various domains on the graphene sheet is nowadays a challenge study and practice.

The pentagonal rings, possibly entering as local bridges over the graphite sheet by reactions like oxidation, amination, or carbene action, will force the geometry of graphene to a bowl-shaped one (Figure 1, the right hand column). The overall positive curvature depends on the bond length of the atoms involved in the bridges, it being as bowl-shaped as the atom covalent radius is smaller (see Table 1). The lattice appears as alternating positive (sumanene) and negative (coronene) curved domains.

MAIN RESULTS

The graphene lattice patterned by CorSu repeat units was designed in the idea of coronene [17] circulene [6:6_6] whose petals were replaced by sumanene [18,19] units, two molecules appearing as domains in fullerenes. Data in Table 1, computed at the PM3 level of theory, show the fragments of the lattice, functionalized by groups containing oxygen, carbon, nitrogen and phosphorus, as relatively stable ones, both as the total energy per atom and HOMO-LUMO geap. The bond lengths are quite reasonable, slightly elongated than the normal values. In comparison, the total energy per atom (in kcal/mol) for C_{60} is -2722.45, while the gap is around 6.59 eV. The bridges defining the pentagonal rings of the sumanene units, will force the planar graphene to adopt a bowl-shaped form and the sp^2 carbon atom is supposed to shift to the sp^3 hybridization. In the whole, the lattices appears as a waved surface, with margins eventually positively curved (Figure 1) or in sent to hyperbolic geometry.

Table 1. Energy and structural data for two fragments of the hypothetical lattice CorSu

	Structure	C_X (A)	TE/HeavyN (Kcal/mol)	HOMO-LUMO Gap (eV)
	CorSu_96 _X			
1	O	1.52	-3271.32	5.950
2	C (CH2)	1.64	-2925.55	6.655
3	N (NH)	1.61	-3007.54	6.740
4	P (PH)	2.06	-2889.53	6.057
	CorSu_198 _X			
5	O	1.52	-3289.57	8.776
6	C (CH2)	1.62	-2889.05	8.603
7	N (NH)	1.58	-2967.23	8.143
8	P (PH)	2.05	-2853.45	6.590

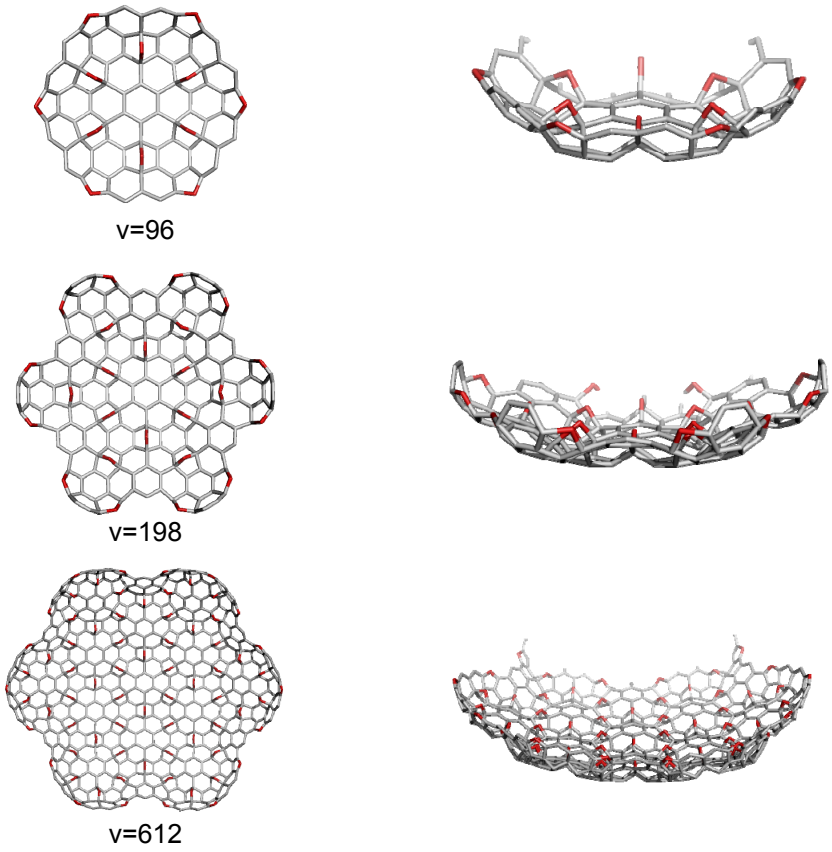

Figure 1. Hexagonal domains in the CorSu graphene sheet: top view (left hand column) and side view (right hand column).

This is the first description of a completely new (hypothetically, yet) lattice, of which functionalization we believe to be soon performed. Of course, the route to such structures is not suggested, remaining as a challenge.

The topology of the lattice is described here in terms of Omega polynomial. Table 2 gives examples for hexagonal (complete) domains.

Table 2. Omega polynomials of hexagonal domains $CorSu_{h,k}$

k	Omega	CI	Atoms	Bonds
0	$24x + 12x^2 + 24x^3 + 3x^6$	18648	96	138
1	$144x + 36x^2 + 156x^3 + 39x^6$	839628	612	918
2	$372x + 60x^2 + 396x^3 + 129x^6$	6013296	1614	2454
3	$708x + 84x^2 + 744x^3 + 273x^6$	22506948	3102	4746
4	$1152x + 108x^2 + 1200x^3 + 471x^6$	60717096	5076	7794

The Omega polynomial for the CorSu lattice of hexagonal domains of $CorSu_{h,k}$ type is:

$$\Omega(CorSu_{h,k}, x) = a_k x + b_k x^2 + c_k x^3 + d_k x^6 .$$

For the starting values, we have $a_0 = 24, b_0 = 12, c_0 = 24, d_0 = 3$. Based on the composition rule, we can deduce the following recurrent formulas:

$$a_{k+1} = a_k + 120 + 108k$$
$$b_{k+1} = b_k + 24$$
$$c_{k+1} = c_k + 132 + 108k$$
$$d_{k+1} = d_k + 36 + 54k$$

After solving these recurrent relations, we get:

$$\Omega(CorSu_{h,k}, x) = (24 + 66k + 54k^2)x + (12 + 24k)x^2 + (24 + 78k + 54k^2)x^3 + (3 + 9k + 27k^2)x^6$$

The number of atoms in the lattice is:

$$v = 96 + 273k + 243k^2 ,$$

while the number of bonds, following (3):

$$e = 138 + 402k + 378k^2 .$$

CI index follows from (4), and is given by the following formula:

$$CI(CorSu_{h,k}) = 18648 + 109764k + 264420\,k^2 + 303912k^3 + 142884k^4$$

Parallelogram domains were also considered; data are given in Table 3.

Table 3. Omega polynomials of parallelogram domains p(a,b)

a	b	Omega	CI	Atoms	Bonds
1	1	$24x + 12x^2 + 24x^3 + 3x^6$	18648	96	138
1	2	$46x + 20x^2 + 50x^3 + 6x^6$	73192	187	272
1	3	$68x + 28x^2 + 76x^3 + 9x^6$	163648	278	406
1	4	$90x + 36x^2 + 102x^3 + 12x^6$	290016	369	540
1	5	$112x + 44x^2 + 128x^3 + 15x^6$	452296	460	674
2	2	$86x + 28x^2 + 94x^3 + 18x^6$	281332	359	532
2	3	$126x + 36x^2 + 138x^3 + 30x^6$	624672	531	792
2	4	$166x + 44x^2 + 182x^3 + 42x^6$	1103212	703	1052
2	5	$206x + 52x^2 + 226x^3 + 54x^6$	1716952	875	1312
3	3	$184x + 44x^2 + 200x^3 + 51x^6$	1383688	784	1178
3	4	$242x + 52x^2 + 262x^3 + 72x^6$	2440696	1037	1564
3	5	$300x + 60x^2 + 324x^3 + 93x^6$	3795696	1290	1950
4	4	$318x + 60x^2 + 342x^3 + 102x^6$	4302468	1371	2076
4	5	$394x + 68x^2 + 422x^3 + 132x^6$	6688528	1705	2588
5	5	$488x + 76x^2 + 520x^3 + 171x^6$	10395448	2120	3226

Let $v(a,b)$ be the number of atoms in the parallelogram domain. We have the following symmetric recurrent formulas

$$v(a,b) = v(a,b-1) + (10 + 81a)$$
$$v(a,b) = v(a-1,b) + (10 + 81b)$$

After solving this second degree recurrent relation, using the starting value $v(1,1) = 96$, it follows:

$$v(a,b) = 81ab + 10a + 10b - 5.$$

Similarly, we can calculate the number of bonds and CI index

$$e(a,b) = 126ab + 8a + 8b - 4$$
$$CI(a,b) = (126ab + 8a + 8b - 4)^2 - 108 + 108(a+b) - 504ab.$$

In case of parallelogram p(a,b) domains, the Omega polynomial equals:

$$\Omega(CorSu_{p(a,b)}, x) = (-2 + 4a + 4b + 18ab)x + (-4 + 8a + 8b)x^2 + (-10 + 8a + 8b + 18ab)x^3 + (6 - 6a - 6b + 9ab)x^6$$

CONCLUSIONS

A new graphene lattice, patterned by CorSu units, was functionalized by groups containing oxygen, carbon, nitrogen and phosphorus, and its stability evaluated at the level of semiempirical method PM3. The small fragments, taken into consideration, showed relatively good stability, as compared with the data for the well-known C_{60}. The topology of the network is described in terms of Omega counting polynomial. Close formulas for calculating the polynomial and the Cluj-Ilmenau index derived from this polynomial were given.

ACKNOWLEDGMENTS

The work was supported in part by the ID_506 Romanian GRANT 2009, and the Research grant 144007 of the Serbian Ministry of Science.

REFERENCES

1. M.V. Diudea, Ed., “Nanostructures, novel architecture”, NOVA, **2005**.
2. M.V. Diudea and Cs. L. Nagy, “Periodic Nanostructures”, Springer, **2007**.
3. L. Carlucci, G. Ciani and D. Proserpio, *Coord. Chem. Rev.*, **2003**, *246*, 247.
4. L. Carlucci, G. Ciani and D. Proserpio, *Cryst. Eng. Comm.*, **2003**, *5*, 269.

5. V.A. Blatov, L. Carlucci, G. Ciani and D. Proserpio, *Cryst. Eng. Comm*., **2004**, *6*, 377.
6. I.A. Baburin, V.A. Blatov, L. Carlucci, G. Ciani and D. Proserpio, *J. Solid State Chem.*, **2005**, *178*, 2452.
7. O. Delgado-Friedrichs and M. O'Keeffe, *J. Solid State Chem*., **2005**, *178*, 2480.
8. V.A. Blatov, O. Delgado-Friedrichs, M. O'Keeffe, and D. Proserpio, *Acta Cryst.,* **2007**, *A63*, 418.
9. P.E. John, A.E. Vizitiu, S. Cigher, M.V. Diudea, *MATCH Commun. Math. Comput. Chem.*, **2007**, *57*, 479.
10. S. Klavžar, *MATCH Commun. Math. Comput. Chem.,* **2008**, *59*, 217.
11. D.Ž. Djoković, *J. Combin. Theory Ser. B*, **1973**, *14*, 263.
12. P.M. Winkler*, Discrete Appl. Math.,* **1984**, *8*, 209.
13. M.V. Diudea, *Carpath. J. Math.,* **2006**, *22*, 43.
14. M.V. Diudea, S. Cigher, P.E. John, *MATCH Commun. Math. Comput. Chem.*, **2008**, *60*, 237.
15. M.V. Diudea, S. Cigher, A.E. Vizitiu, M.S. Florescu, P.E. John, *J. Math. Chem.*, **2009**, *45*, 316.
16. Cs. L. Nagy, M.V. Diudea, *Nano Studio software*, Babes-Bolyai Univ., **2009**.
17. K. Yamamoto, *Pure Appl. Chem.,* **1993**, *65*, 157.
18. H. Sakurai, T. Daiko, T. Hirao, *Science,* **2003**, *301*,1878.
19. H. Sakurai, T. Daiko, H. Sakane, T. Amaya, T. Hirao, *J. Am. Chem. Soc.*, **2005**, *127*, 11580.