STUDIA UBB. CHEMIA, LV, 4, 2010

DIAMOND D_5, A NOVEL ALLOTROPE OF CARBON

MIRCEA V. DIUDEA[*]

ABSTRACT. Design of a hypothetical crystal network, consisting mostly of pentagon rings and called diamond D_5, is presented. It is shown that the seed and repeat-units, as hydrogenated species, show good stability, compared with that of C_{60} fullerene, as calculated at three levels of theory (PM3, HF/6-31G(d,p), B3LYP/6-31G). The topology of the network is described in terms of the net parameter.

Keywords: *diamond D_5; nano-dendrimer; multi-tori; crystal-like network.*

INTRODUCTION

The nano-era, a period starting, since 1985 with the discovery of C_{60}, is dominated by the carbon allotropes, studied for applications in nano-technology. Among the carbon structures, fullerenes (zero-dimensional), nanotubes (one dimensional), graphene (two dimensional), diamond and spongy nanostructures (three dimensional) were the most studied [1,2]. Inorganic compounds also attracted the attention of scientists. Recent articles in crystallography promoted the idea of topological description and classification of crystal structures [3-7].

Diamond D_6, the classical, beautiful and useful diamond has kept its leading interest among the carbon allotropes, even as the newer "nano" varieties [8-10]. Along with electronic properties, the mechanical characteristics appear of great importance, as the composites can overpass the resistance of steel or other metal alloys. A lot of efforts were done in the production and purification of "synthetic" diamonds, from detonation products [11-14].

Dendrimers are hyper-branched nano-structures, made by a large number of (one or more types) substructures called monomers, synthetically joined within a rigorously tailored architecture [15-17]. They can be functionalized at terminal branches, thus finding a broad pallet of applications in chemistry, medicine, etc [18,19].

Multi-tori MT are structures of high genera [1,2,20], consisting of more than one tubular ring. They are supposed to result by self-assembly of some repeat units (*i.e.*, monomers) which can be designed by opening of cages/ fullerenes or by appropriate map/net operations. Such structures can appear in spongy carbons or in zeolites [20]. Spongy carbons have been recently synthesized [21,22].

---

[*] *Faculty of Chemistry and Chemical Engineering, "Babes-Bolyai" University, 400028 Cluj-Napoca, Romania, mpop@chem.ubbcluj.ro; diudea@gmail.com*

There are rigid monomers that can assembly in dendrimers, but the growing process stops rather at the first generation. At a second generation, yet the endings of repeat units are not free any more, they fit to each other, thus forming either an infinite lattice, if the unit symmetry is octahedral or a spherical multi-torus, if the unit symmetry is tetrahedral. The last one is the case of structures previously discussed in refs [23,24].

RESULTS AND DISCUSSION ULTI-TORUS DESIGN AND STABILITY

A tetrapodal monomer M_1(Figure 1, left), designed by $Trs(P_4(T))$ sequence of map operations [25-28] and consisting of all pentagonal faces, can self-arrange to form a dendrimer M_5, at the first generation stage (Figure 1, right).

Figure 1. Tetrapodal unit designed by $Trs(P_4(T))$ and the corresponding dendrimer, at 1st generation stage

The "growing process" is designed occurring by identifying the trigonal faces of two opposite M_1 units; at the second generation, six pentagonal hyper-cycles are closed, as in molecule M_{17}, Figure 1.

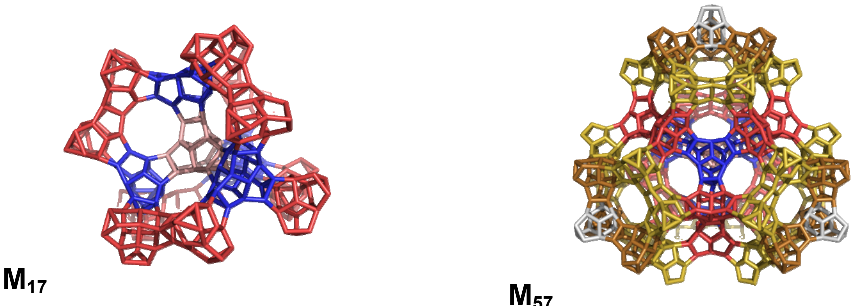

Figure 2. Dendrimer at 2nd (left) and 5th (right) generation stage; M_{57}=4S_MT; v=972; e=1770; f_5=684; g=58 (infinite structure); adding f_3=40, then g=38 (finite structure)

The process is imagined as a "dendrimer growing", and it is limited here at the fifth generation (Figure 2), when a tetrahedral array results: 4S_MT= M_{57}.

Multi-tori herein considered can be viewed either as infinite (*i.e.*, open) structures or as closed cages; then, it is not trivial to count the number of simple tori (*i.e.*, the genus *g*) in such complex structures.

The Euler's formula [29]: $v-e+f=2(1-g)$, where *v*, *e* and *f* are the number of vertices/atoms, edges/bonds, and faces, respectively, is applicable only in case of single shell structures. In multi shell structures, we modified [30] the Euler formula as: $v-e+r-p(s-1)=2(1-g)$, where *r* stands for the number of hard rings (*i.e.*, those rings which are nor the sum of some smaller rings), *p* is the number of smallest polyhedra filling the space of the considered structure while *s* is the number of shells. In case of an infinite structure, the external trigonal faces are not added to the total count of faces/rings. The calculated *g*-values are given in figures.

The number of tetrapodal monomers, added at each generation, up to the 5th one, realized as M_{57}, is: 1; 4; 12, 24, 12, 4. The connections in M_{57} are complex and to elucidate the large structures up to the fifth generation, the reduced graph drawing (Figure 3) was needed [24].

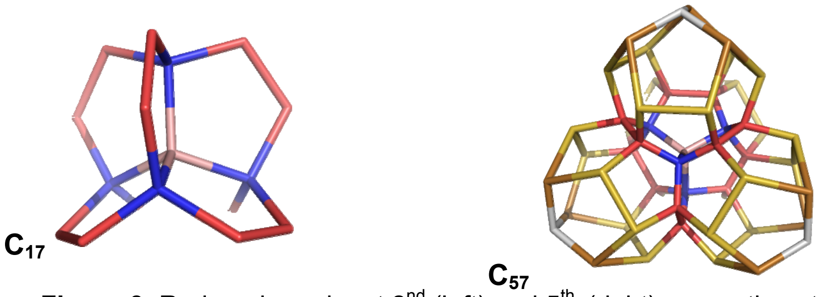

Figure 3. Reduced graphs at 2nd (left) and 5th (right) generation stage; C_{57}: v=57; e=94; r_5=42; g=0.5; $R(x)=42x^5+82x^9+144x^{10}$

The structure C_{17} (Figure 3, left) we call the "seed" of all the hereafter structures. The structure C_{57} (Figure 3, right) corresponds to 4S_MT, and is equivalent to 4 "condensed" dodecahedra, sharing a common point. By considering this common point as an internal shell *s*, the modified [30] Euler formula will give (for v=57; e=94; r=42; p=4 and s=2) a (non-integer) genus g=0.5. The ring polynomial R(*x*) is also given, at the bottom of Figure 3.

Energetic data, calculated at three levels of theory (Table 1) show a good stability of the structures shown in Figure 3 (as hydrogenated species), in comparing to C_{60}, the reference structure in Nano-science. Differences in HOMO-LUMO gap (in eV) in favor of the new (all sp^3 carbon atoms) structures, are just expected for hydrogenated (stable) species while the total energies are close comparable. The corresponding fullerene-like (containing both sp^3 and sp^2 carbon atoms) C_{57} is close to C_{60} as total energy while the gap vary, function of the considered approach: in PM3 and B3LYP the gap is lower for C_{57} than for C_{60} while in Hartree-Fock HF this parameter is in favor of C_{57}. The above structures represent energetic minima, as shown by the simulated IR vibrations. All-together, these data reveal the proposed structures as pertinent candidates to the status of real molecules.

Table 1. Data on the structures in Figure 3 (HOMO-LUMO gap in eV, heat of formation Hf in kcal mol^{-1}, and total energy E_{tot} in a.u.) for the intermediate structures in building the C_{57} multi-cage, calculated at the PM3, HF/6-31G(d,p), B3LYP/6-31G(d,p) levels of theory; C_{60} is taken as reference structure.

Struct	Sym	PM3		HF		B3LYP	
		Gap	Hf	Gap	E_{tot}	Gap	E_{tot}
$C_{17}H_{12}$	T_d	10.53	131.66	12.99	-650.66	6.04	-654.92
$C_{57}H_{40}$	T_d	13.438	-49.11	14.270	-2181.99	7.365	-2170.67
C_{57}	D_{2d}	6.432	1497.92	7.574	-2156.98	1.888	-2196.27
C_{60}	I_h	6.596	810.82	7.420	-2271.83	2.761	-2286.17

DIAMOND D_5 NETWORK

A monomer C_{81}, derived from C_{57} and consisting of four closed C_{20} units and four open units, and its mirror image (Figure 4) is used to build the alternant network of the spongy diamond SD_5 (Figure 5).

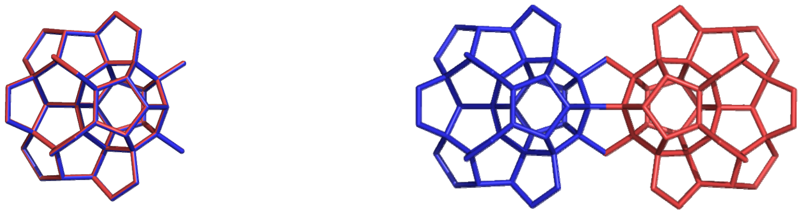

Figure 4. Monomer C_{81} unit (left-up), and its mirror image-pair (right-up); the repeating units of the spongy diamond SD_5 network.

The PM3 optimized structure $SD_5(2,2,2)=C_{600}H_{160}$ shows: heat of formation HF=4492.414 kcal/mol; heat of formation per heavy atoms HF/HA=7.487; Homo-Lumo-Gap=8.457 eV. In comparison, HF/HA (C_{60})=13.514 kcal/mol, thus justifying future studies (see also Table 1).

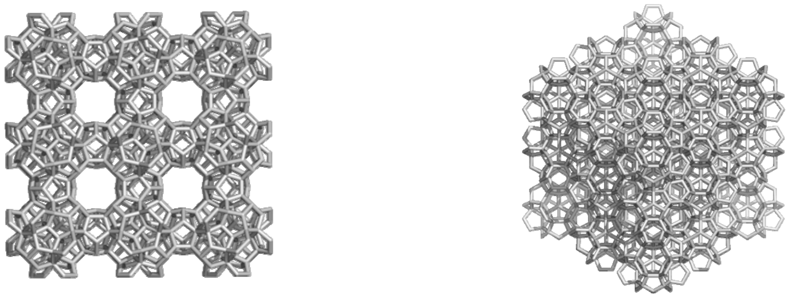

Figure 5. Spongy diamond SD_5 (3,3,3) network: top (left) and corner (right) views.

Formulas enabling the calculation of net parameter (vertices *v*, edges *e*, and the number of monomers *m* in a cubic domain), the ring polynomial *R*(*x*), number of carbon atoms C(sp^2) and C(sp^3) and their ratios together with the limits of these quantities (when *k* trends to infinity) are presented in Table 2, function of *k* – the number of monomers along the edge of cubic domain. The network in Figure 5 is related to the P-type crystal proposed by Mackay for the Schwarzites [31].

Table 2. Topology of spongy diamond SD_5 (C_{81}) network

	Formulas
1	$v(\mathrm{SD}_5) = 3k^2[27+23(k-1)] = 69k^3+12k^2$; $e(\mathrm{SD}_5) = 130k^3$; $m(\mathrm{SD}_5) = k^3$
2	$R(x) = ax^5 + bx^9 + cx^{10}$ $a = 6k^2[9+11(k-1)]$; $b = 6k^2[18+26(k-1)]$; $c = 6k^2[27+44(k-1)]$
3	$C(sp^3) = 53k^3 - 12k^2$
4	$C(sp^3\%) = (53k^3-12k^2)/(69k^3+12k^2)$ $\lim_{k\to\infty}(C(sp^3\%)) = 53/69$; 0.768116

Notice that there exist other diamond structures, either as real (Lonsdaleite, a rare stone of pure carbon discovered at Meteor Crater, Arizona, in 1967) or hypothetical [2,33] ones.

The structure C_{17}, has the skeleton of centrohexaquinane, and was synthesized (so far) as centrohexaindane [34], or C-trioxa-s-hexaquinane [35]

CONCLUSIONS

A new, yet hypothetically, carbon allotrope, called diamond D_5, was designed by using the structure C_{81} as the repeating unit (for the spongy form SD_5). Diamond D_5 was theorized here for the first time in literature (even the origins of this completely new idea were presented in two previous articles [23,24]). The geometric and energetic arguments/proofs, summarily presented here, as well as the *dense* D_5 diamond network will be completed in further papers [36,37].

We expect the same mechanical, thermal, electrical, lubricating, catalyst support, biological, etc. properties as those found for the nano-diamond D_6.

ACKNOWLEDGMENTS

The work is supported by the Romanian CNCSIS-UEFISCSU project number PN-II IDEI 129/2010. The author wish to thank to Dr. Csaba L. Nagy for quantum chemical calculations.

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, *Cryst. Eng. Comm.*, **2003**, *5*, 269.
4. V.A. Blatov, L. Carlucci, G. Ciani and D. Proserpio, *Cryst. Eng. Comm.*, **2004**, *6,* 377.
5. I.A. Baburin, V.A. Blatov, L. Carlucci, G. Ciani and D. Proserpio, *J. Solid State Chem.*, **2005**, *178*, 2452.
6. O. Delgado-Friedrichs and M. O’Keeffe, *J. Solid State Chem.*, **2005**, *178*, 2480.
7. V.A. Blatov, O. Delgado-Friedrichs, M. O’Keeffe, and D. Proserpio, *Acta Cryst.*, **2007**, *A63*, 418.
8. E. Ōsawa, *Diam. Rel. Mat*. **2007**, *16*, 2018.
9. E. Ōsawa*, Pure Appl. Chem.*, **2008**, *80*, 1365.
10. V.N. Mochalin and Yu. Gogotsi, *J. Am. Chem. Soc.*, **2009**, *131*, 4594.
11. P.S. DeCarli, J.C. Jamieson, *Science*, **1961**, *133*, 1821.
12. A.E. Aleksenski, M.V. Baidakova, A.Ya. Vul’, V.Yu. Davydov, Yu.A. Pevtsova, *Phys. Solid State*, **1997**, *39*, 1007.
13. A. Krüger, F. Kataoka, M. Ozawa, T. Fujino, Y. Suzuki, A.E. Aleksenskii, A.Ya. Vul’, E. Ōsawa, *Carbon*, **2005**, *43*, 1722.
14. O.A. Williams, O. Douhéret, M. Daenen, K. Haenen, E. Ōsawa, M.M. Takahashi, *Chem. Phys. Lett.*, **2007**, *445*, 255.
15. M.V. Diudea and G. Katona, in: Newkome, G.A. Ed., *Advan. Dendritic Macromol.* **1999**, *4*, 135.
16. G.R. Newcome, V.K. Gupta, G.R. Baker, Z.-Q.Yao, *J. Org. Chem.* **1985**, *50*, 2003.
17. D.A. Tomalia, *Aldrichimica Acta,* **1993**, *26*, 91.
18. M. Tang, C.T. Redeman, F.C. Szoka, Jr., *Bioconjugate Chem.,* **1996**, *7*, 703.
19. B.F. Pan, D.X. Cuị, P. Xu, T. Huang, Q. Li, R. He, and F. Gao, *J. Biomed. Pharmaceut. Eng.*, **2007**, *1*, 13.
20. M.V. Diudea, *Nanomolecules and Nanostructures-Polynomials and Indices*, MCM, No. 10, Univ. Kragujevac, Serbia, **2010**.
21. G. Benedek, H. Vahedi-Tafreshi, E. Barborini, P. Piseri, P. Milani, C. Ducati, and J. Robertson, *Diamond Relat. Mater.*, **2003**, *12*, 768.
22. E. Barborini, P. Piseri, P. Milani, G. Benedek, C. Ducati, and J. Robertson, *Appl. Phys. Lett.*, **2002**, *81*, 3359.
23. M.V. Diudea, A. Ilić, *J. Comput. Theoret. Nanosci.,* **2011**, *8*, 000-000.
24. M.V. Diudea, Int. J. Chem. Model., **2010** (accepted).
25. M.V. Diudea, M. Ştefu, P.E. John, and A. Graovac, *Croat. Chem. Acta,* **2006**, *79*, 355.
26. M.V. Diudea, *J. Chem. Inf. Model.,* **2005**, *45,* 1002.
27. M.V. Diudea, *Forma* (Tokyo), **2004**, *19* (3), 131.
28. M. Stefu, M.V. Diudea and P.E. John, *Studia Univ. Babes-Bolyai Chemia*, **2005**, *50* (2), 165.

29. L. Euler, *Novi Comm. Acad. Scient. Imp. Petrop.*, **1758**, *4*, 109.
30. M.V. Diudea and C.L. Nagy, *MATCH Commun. Math. Comput. Chem.*, **2008**, *60*, 835.
31. A.L. Mackay and H. Terrones, *Nature*, **1991**, *352*, 762.
32. Zh. Chen, T. Heine, H. Jiao, A. Hirsch, W. Thiel, and P. von Rague Schleyer, *Chem. Eur. J.*, **2004**, *10*, 963.
33. T. Sunada, *Notices AMS*, **2008**, *55*, 208.
34. D. Kuck, *Pure Appl Chem*., **2006**, *78*, 749.
35. L.A Paquette, M. Vazeux, *Tetrahedron Lett*., **1981**, *22*, 291.
36. M.V. Diudea, Cs.L. Nagy, *Diam. Rel. Mat.*, **2010** (submitted).
37. M.V. Diudea, Cs.L. Nagy, *Carbon*, **2011** (submitted).