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OCTAHEDRAL CNT JUNCTIONS AS P-TYPE NETWORKS

VIRGINIA BUCILA[a], MONICA STEFU[a] AND BEATA SZEFLER[b*]

ABSTRACT. Octahedral carbon nanotube CNT junctions designed by map operations are extended to 3D periodic structures in the Euclidean space, thus P-type surface being decorated with a variety of polyhedral motifs. They can be seen as nets of spongy sp^2 covalently bonded carbon atoms or nets of aluminosilicates, called zeolites. Topological, energetic and crystallographic aspects are discussed.

Keywords: ***3-****periodic structures, octahedral junctions, cubic network,*

INTRODUCTION

A covalent lattice, consisting of sp^2 carbon atoms, can be embedded in a triple periodic minimal surface, particularly in a P-type surface. Carbon allotropes, having the structure of a simple cubic network, were named *periodic schwarzites*, in the honor of H. A. Schwarz [1,2], who first investigated, in the early nineteen century, their differential geometry. The nodes of the cubic network can be assimilated to nanotube junctions and can be decorated by using some map operations. A map *M* is a combinatorial representation of a closed surface (i.e., covering, tessellation). Map operations are some topological operations enabling generation and/or transformation of a given map into new maps.

Recall Euler's basic relations in polyhedra [3,4]: $\sum d\, v_d = 2e$ and $\sum s\, f_s = 2e$, where e are the number of edges, v_d are the number of vertices of degree *d* and and f_s the number of *s*-gonal faces /faces of size s. The two relations are joined into a third formula: $v - e + f = \chi(M) = 2(1-g)$ with χ being the Euler *characteristic* and *g* is the genus [5] (*i.e.*, the number of simple tori to which a given structure can be reduced, or the number of structure's holes; *g*=0 for the sphere or the plane and g=1 for a simple torus).

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Positive/negative χ values indicate positive/negative curvature of a lattice. An embedding is a representation of a graph on a closed surface such that no crossing lines appear [5].

In view of generating the desired nanotube junctions, we present here only four composite map operations, the reader being invited to consult some related references [6,7].

Leapfrog Le [8,9], can be obtained by two successive operations:

$$Le(M) = Du(P_3(M)) = Tr(Du(M))$$

where *Du* is the Poincaré dual, P_3 is the triangulation while *Tr* is the truncation. The transformed map parameters are: *Le*(*M*); $v = s_0 f_0 = d_0 v_0$; $e = 3e_0$; $f = v_0 + f_0$ with the subscript zero denoting the parameters in the parent map. The number of vertices in *Le*(*M*) *is* d_0 times larger than in the parent map, irrespective of its tessellation. Since in trivalent maps *Le* multiplies 3-times the number of original vertices, it is also called the *tripling* operation. *Le* rotates the parent *s*-gonal faces by π/*s*. The most common example is the leapfrogging of dodecahedron Do: *Le*(Do)=C_{60}.

Quadrupling Q or *chamfering* [8,10-12**]** is achieved by the following sequence:

$$Q(M) = E_{-}(Tr_{P_3}(P_3(M)))$$

where E_{-} means the (old) edge deletion of the truncation Tr_{P3} of each vertex introduced by P_3 capping. The vertex multiplication ratio in a *Q*-transformed map is d_0 + 1 irrespective of the original map tessellation: *Q*(*M*); $v = (d_0 + 1)v_0$; $e = 4e_0$; $f = f_0 + e_0$.

Vertex multiplication factor *m* induced by a map operation, on a trivalent map, is calculated by the Goldberg's polynomial [13]: $m = (a^2 + ab + b^2); a \geq b; a + b > 0$, with *a*, *b* being integers. The *m* factor is also related to the formula giving the volume of truncated pyramid, of height *h*: *V* = *mh*/3, coming from the ancient Egypt. For *Le*(1,1); *m*=3 while for *Q*(2,0); *m*=4.

*Septupling S*1 is a third composite operation [14], with S_1(2,1)=7. It was also called *Capra Ca* (the goat, in Romanian [15]), corresponding to the *leapfrog* English children game. S_1 is achieved by truncation Tr_{P5} of the face centered vertices introduced by P_5 pentangulation (see above the definition for *Q*(M)). Note that P_5 involves an E_2 (*i.e.*, edge trisection). This operation preserves the original vertices while the parent *s*-gonal faces are twisted by π/2*s*. It can be written as:

$$S_1(M) = Ca(M) = Tr_{P_5}(P_5(M))$$

The vertex multiplication ratio in $S_1(M)$ is $2d_0 + 1$ irrespective of the original map tiling: $S_1(M)$; $v_1 = v_0 + 2e_0 + s_0 f_0 = (2d_0 + 1)v_0$; $e_1 = 7e_0$; $f_1 = s_0 f_0 + f_0$.

S_1 insulates any parent face by its own hexagons, while *Le* or *Q* introduce hexagons that are shared between two parent faces. Figure 1 illustrates some nanostructures designed by map operations.

Le(Cube) ***N***=24 Q(Cube) ***N***=32

Ca(Cube); ***N*** =56 S$_2$(Cube) ***N*** = 56

Figure 1. Four composite operations applied to the Cube

S_1 can continue with an E_n homeomorphic operation on the edges bounding the parent-like faces (*i.e.*, those resulted by Tr_5), thus resulting open maps with all polygons of the same (6+*n*) size. This last operation is called the *Opening* Op_n operation [16,17]. The transformed map parameters are as follows: $Op(S_1(M))$; $v(Op(S_1)) = v + s_0 f_0 = (3d_0 + 1)v_0$; $e(Op(S_1)) = 9e_0$ and $f(Op(S_1)) = f - f_0 = s_0 f_0$.

Septupling S_2 [14] is the twin operation of S_1, because the two $S_k(M)$ transformed maps form complementary lattices (see below). It can be achieved by putting four vertices on each edge of the parent map *M* (*i.e.*, the E_4 operation) and next join these new vertices in the order (-1, +3):

$$S_2 = J_{(-1,+3)}(E_4(M))$$

The transformed map parameters are identical to the S_1 operation: $S_2(M)$ =$S_1(M)$; $v=(2d_0+1)v_0\,;e=7e_0\,;f=s_0f_0+f_0$. It insulates the parent faces by pentagon triples and the transformed maps are non-chiral ones. However, chirality can be introduced by the opening operation *Op*$_{2a}$, realized by two points put on alternative edges of a boundary, thus getting twice folding of the parent faces. The transformed map parameters are:

$$Op_{2a}(S_2(M))\,;v_{Op(S_{2a})}=(4d_0+1)v_0\,;e_{Op(S_{2a})}=11e_0\,;f_{Op(S_{2a})}=s_0f_0\,.$$

An opening operation $Op_1(S_2(M))$ is also known [6, 14].

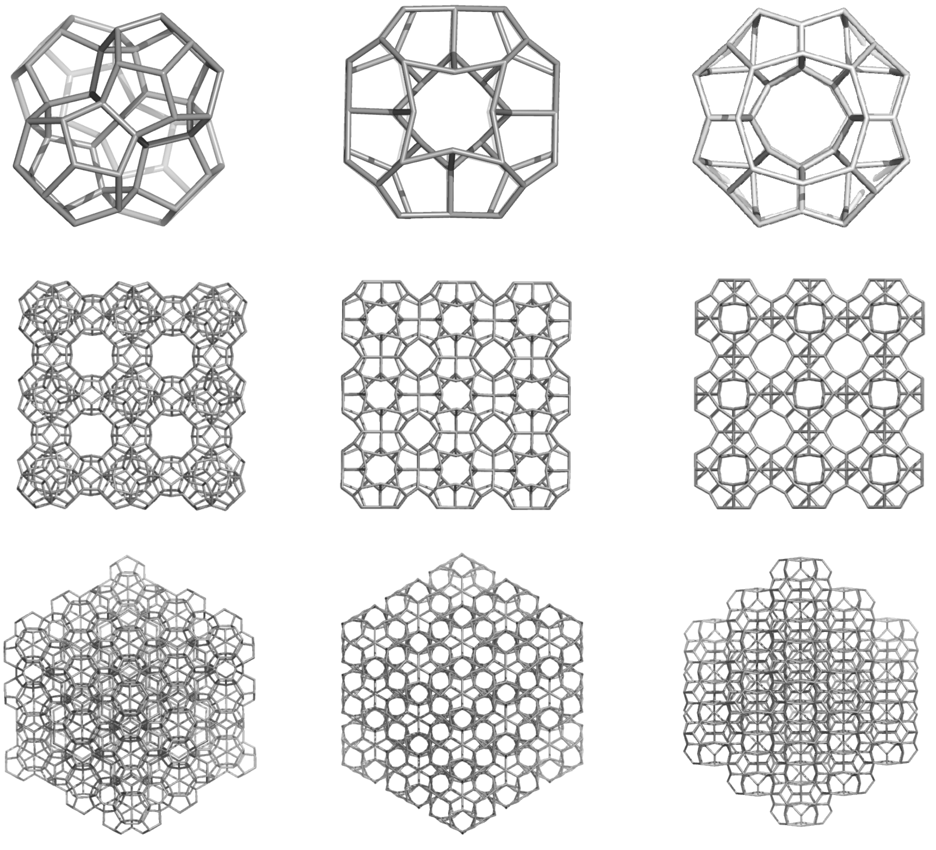
Sequences of such operations enable the decoration of various surfaces, with both positive and negative curvature. Graphite as reference, has zero curvature. The negative curvature can be induced by 7-size or larger rings, while rings of size 5 or less generate positive curvature. Negatively curved structures can form infinite periodic networks. A tessellation made by a single type of polygons is called Platonic; when two types of polygonal faces exist, the covering is called Archimedean [7].

Multi-tori [18] are complex structures consisting of more than one single torus (i.e., hyper ring). They can result by self-assembly of some repeating units/monomers, formed by spanning of cages/fullerenes and can appear in spongy carbon [19] and in natural zeolites [20], as well. Multi-tori can grow either spherically (3D /three-dimmensional) or linearly, in forming arrays of various complexity [7]. The above operations have been performed by the original software CVNET [21]

NET CONSTRUCTION

The hypothetical carbon cubic networks herein discussed were designed by joining (with the Nano Studio original software [22]) opened octahedral carbon nanotube CNT junctions. Open objects can be designed by the *Opening Op* operation, applied consecutively to the regular map operations. The most used map operations are: *Leapfrog* – *Le*$_{1.1}$, *Quadrupling* – $Q_{2.0}$, *Capra* – *Ca*$_{2.1}$, which are applied to the Cube or Cube-derived maps for obtaining octahedral junctions necessary to build a P-type network.

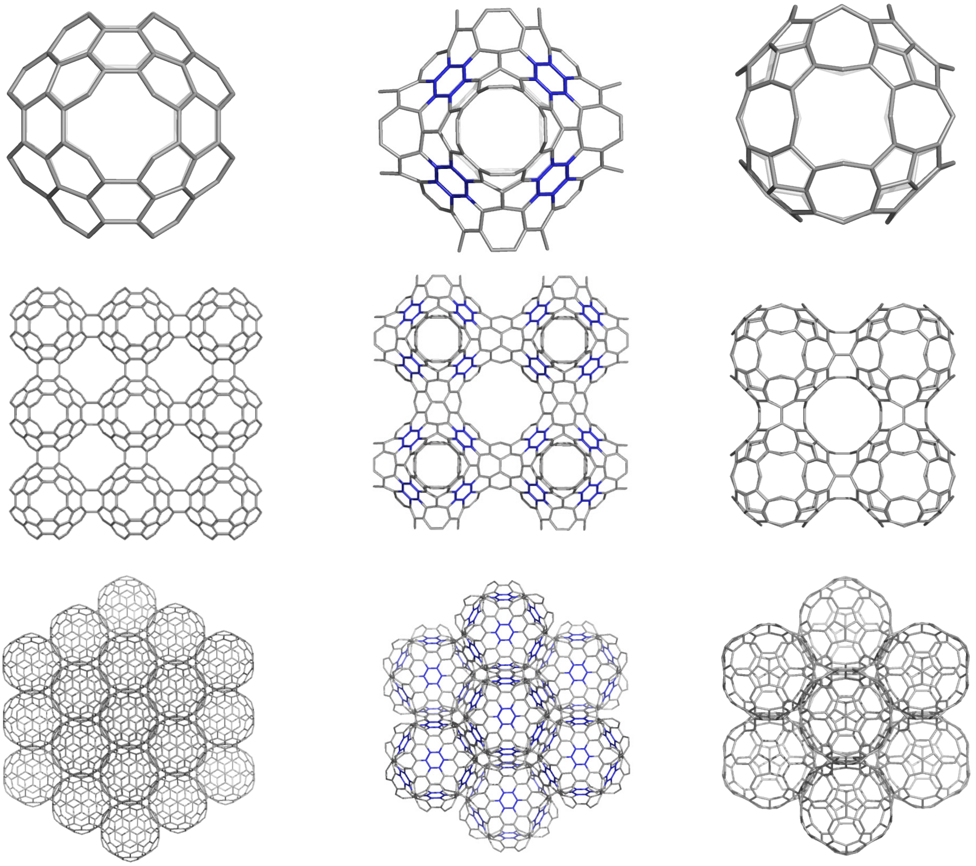
Figures 2–5 present 10 new 3-periodic structures, designed at TOPO GROUP Cluj. Crystallographic investigation was performed by an original software, called “Atom”, developed at our group in collaboration with Prof. Davide Proserpio, University of Milan, Italy [23].



diu1 diu2 diu3

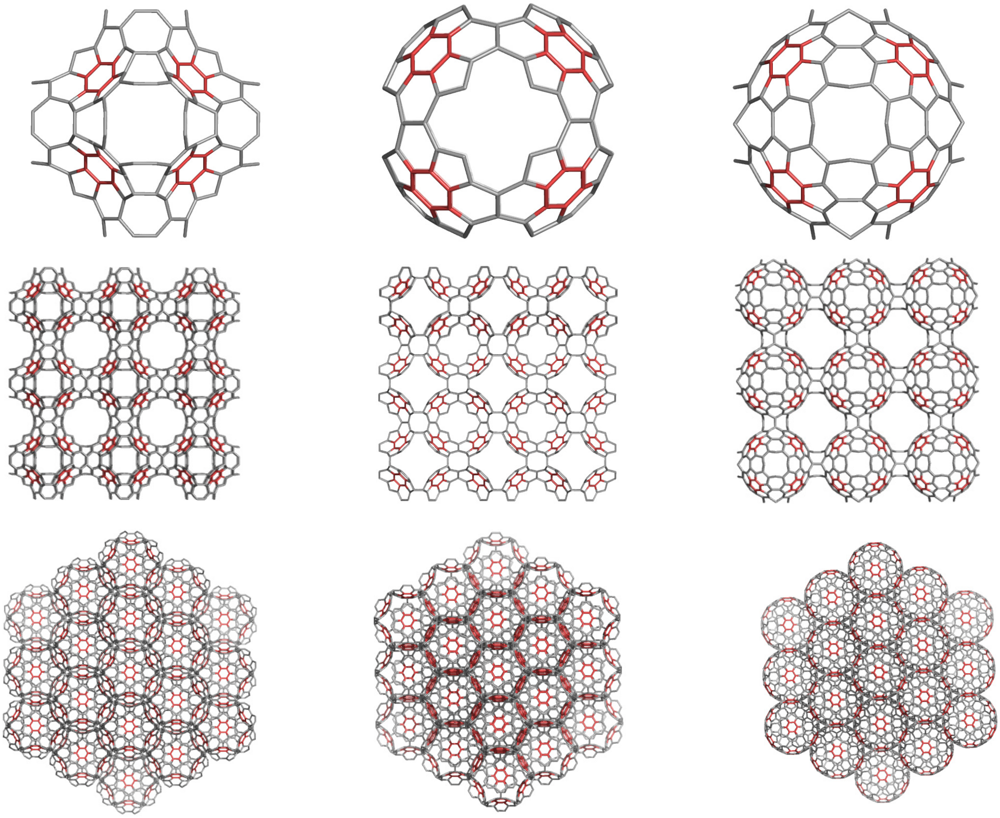
Figure 2. The cubic networks diu1, diu2, diu3, denoted by Diudea’s name

The structures were noted by the shortened Diudea’s name, *diu*. The crystallographic description of these hypothetical crystal networks is given in Appendix.



diu4 diu6 diu7

Figure 3. The cubic networks diu4, diu6, diu7



diu9 diu10 diu11

Figure 4. The cubic networks diu9, diu10 and diu11

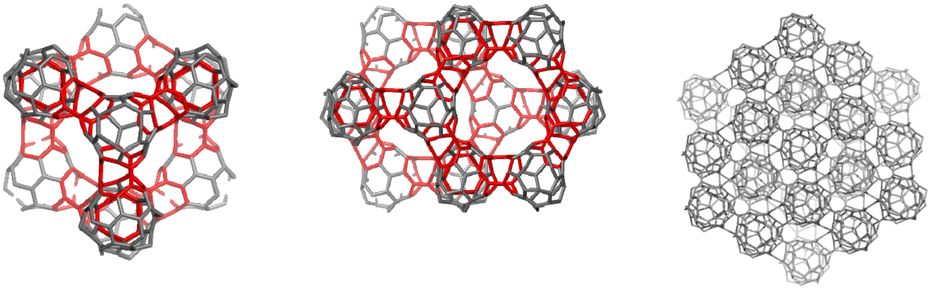


Figure 5. The diamondoid network diu5

STABILITY OF STRUCTURES

Evaluating the cohesive energy of the hypothetical crystal networks is over the aim of this paper. However, for some small constructive units we computed single point energies on optimized geometries at Hartree-Fock HF (HF/6-31G**) level of theory. The calculations were performed in gas phase by Gaussian 09 [24]. It was necessary to use relatively large computational effort for this examination, due to the size of the structures. Data are listed in Table 1.

Table 1. Total energy E_{tot} per atom (kcal/mol) and HOMO-LUMO HL Gap, at Hartree-Fock HF (HF/6-31G**) level of theory for some units of some Sumanene-based structures.

Structure	Structural unit	No. C atoms	HF/6-31G(d,p) (au)	E_{tot}/atom (au/mol)	HF_Gap (eV)
1	C_{60}	60	-2271.830	-37.864	7.418
2	diu9	216	-8206.401	-37.993	6.442
3	diu10	168	-6389.018	-38.030	6.637
4	diu11	192	-7298.367	-38.012	6.044

As a reference structure, we considered C_{60}, the most referred structure in Nanoscience. This test of stability was done to support the idea that sumanene, a real molecule [25,26], can be used to synthesize structural units for more elaborated nanostructures (e.g. diu9 to diu11), eventually called “ordered Schwarzites”, embedded in the P-surface. From Table 1 it is clear that such units show a stability comparable to the well-known C_{60} reference structure, thus being possible candidates for laboratory synthesis.

CONCLUSIONS

Operations on maps are useful tools in the design of polyhedral nanostructures. Octahedral carbon nanotube junctions can be extended to 3D periodic nanostructures in the Euclidean space, thus decorating the P-type surface by a variety of polyhedral motifs. Topological, energetic and crystallographic aspects were discussed. For some finite small units, data suggest a good stability, thus being promising for future laboratory synthesis.

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M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N.J. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian Inc Wallingford CT, Revision A.1, 2009.

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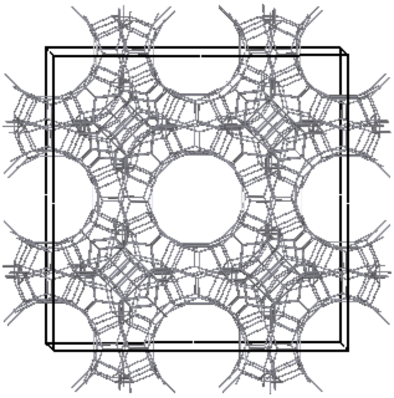
APPENDIX

In the following, the networks are represented as given by Topos computer program, (on left), where the repetitive cell/unit is enclosed in squares, and by HyperChem program (on right). Before the figures, the crystalographic Topos data are given.

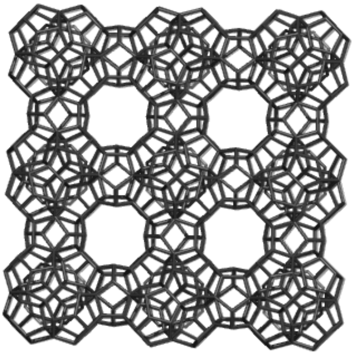
1. NEW: diu1 (D_5 diamond, spongy) D_{5spo}

Point symbol for net: $(5^3)16(5^5.8)36(5^6)17$
3,3,4,4,4,4,4-c net with stoichiometry (3-c)16(4-c)53; 7-nodal net
VS [5.5.5] [5.5.5] [5.5.5.5.5.12] [5.5.5.5.5.5] [5.5.5.5.5.12_2] [5.5.5.5.5.5] [5.5.5.5.5.5]
New topology



333cell 333C20_1755_ICIF

Diudea's name **diu1**

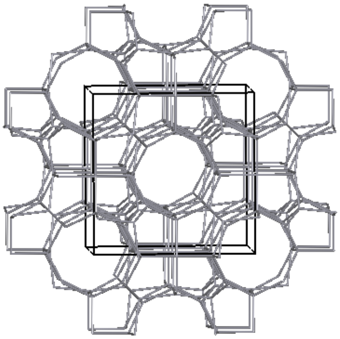


333C20_1755_ICIF

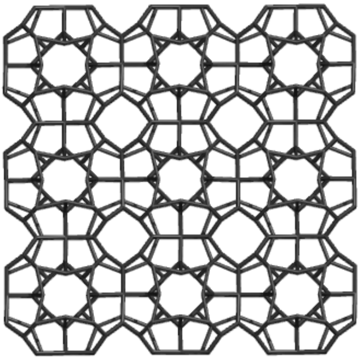
D_{5spo}

2. NEW: diu2 (Cube, Polygonal P4, Unit, co-net, hexagon 6, X cut edges) CP4UCo6X

Point symbol for net: $\{6^3\}4\{6^4.8^2\}3\{6^5.8\}6$
3,4,4-c net with stoichiometry (3-c)4(4-c)9; 3-nodal net
VS $[6.6.6]$ $[6.6.6.6.6_2.8_2]$ $[6_2.6_2.6_2.6_2.8.8]$
New topology



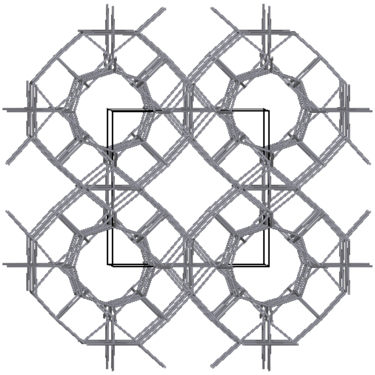
p4u_corecell P4U_Core_6E_333B
Diudea's name diu2



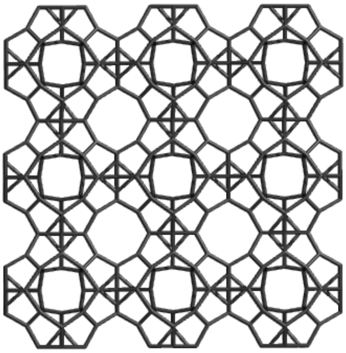
P4U_Core_6E_333B
CP4UCo6X

3. NEW: (Cube, Polygonal P4, Unit, co-net, hexagon 6, X cut edges, face 4) CP4UCo6X4

Point symbol for net: $\{4.6^4.8\}2\{4.6^5\}2\{6^2.8\}2\{6^3\}2\{6^4.8^2\}\{6^5.8\}4$
3,3,4,4,4,4,4,4,4-c net with stoichiometry (3-c)4(4-c)9; 9-nodal net
VS $[6_2.6_2.8_2]$ $[6.6.6]$ $[4.8_2.6_2.6_2.6_2.6_2]$ $[4.8_2.6.6.6.6]$ $[6_2.6_2.6_2.6_2.8.16_2]$ $[4.6_2.6.6.6.6]$ $[6.6.6.6.6_2.8_2]$ $[6.6.6.6.6_2.8]$ $[4.6_2.6.6.6.6]$
New topology



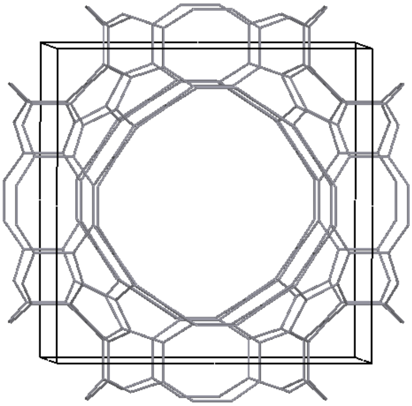
p4u_core_6x6cell
Diudea's name Diu3



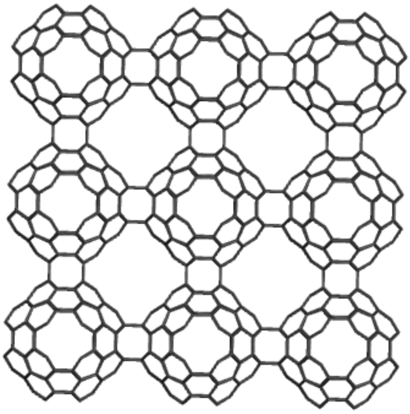
P4U_Core_6x6_333_1620
CP4UCo6X4

4. NEW (Cube, hexagon triple) diu4=C3Hex

Point symbol for net: $\{6.8^2\}3\{6^2.8\}6\{6^3\}4$
3,3,3,3-c net with stoichiometry (3-c)13; 4-nodal net
VS [6.8.8] [6.6.8] [6.6.6] [6.6.6]
New topology



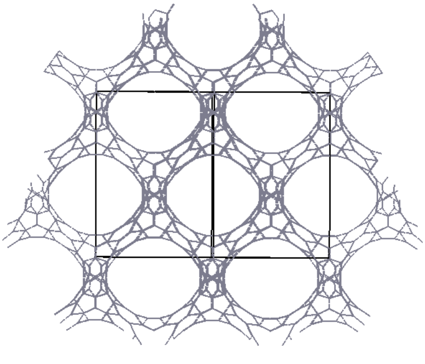
c3hexcell C3Hex_333
Diudea,s name diu4



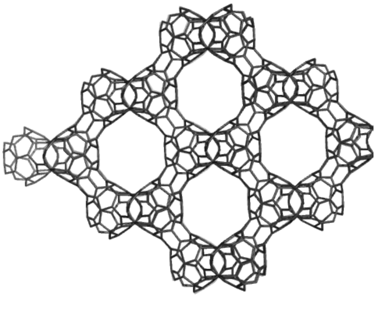
C3Hex_333
C3Hex

5. NEW diu5= T3HextwDia chiral net derived as decoration of dia net (Tetrahedron, hexagon triple, twisted)

Point symbol for net: $\{6.8^2\}3\{6^2.8\}6\{6^3\}$
3,3,3,3-c net with stoichiometry (3-c)10; 4-nodal net
VS [6.6.8] [6.6.6] [6.8.8] [6.6.8]
New topology



t3cell
Diudea,s name diu5

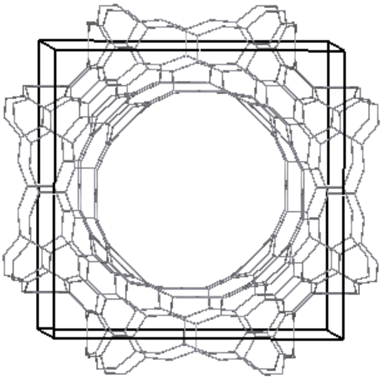


T3HextwDia_222_1760

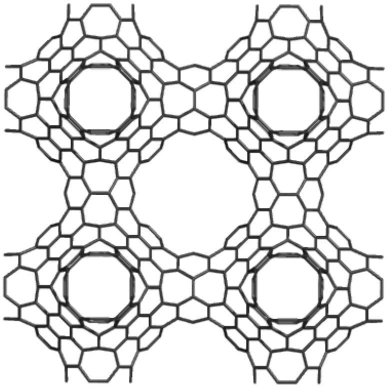
T3HextwDia

6. NEW (Cube,Coronene) diu6=CCor216

Point symbol for net: $(6.7^2)(6^2.7)5(6^3)2$
3,3,3,3,3-c net with stoichiometry (3-c)8; 5-nodal net
VS [6.6.7] [6.6.7] [6.6.7] [6.6.6] [6.7.7]
New topology



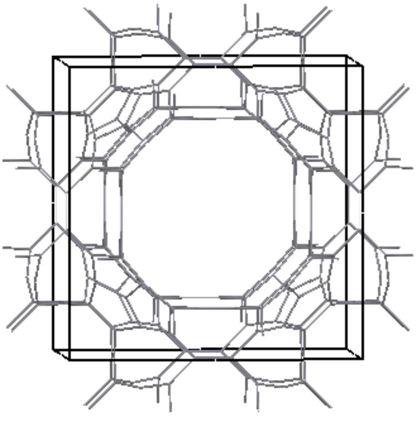
corcell Cor_268_111_2x2x2
Diudea,s name diu6



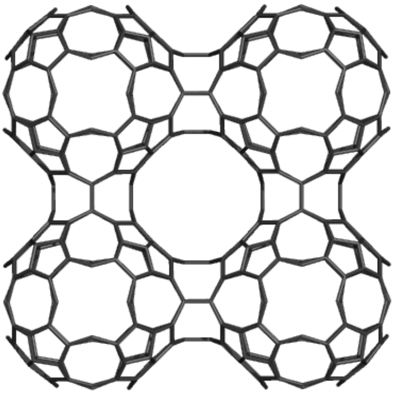
Cor_268_111_2x2x2
CCor216

7. NEW diu7=MoZOp

Point symbol for net: $(5.8^2)6(5^2.8)3(5^3)(8^3)3$
3,3,3,3-c net with stoichiometry (3-c)13; 4-nodal net
VS [5.5.8] [5.8.8] [5.5.5] [8.8.8]
New topology



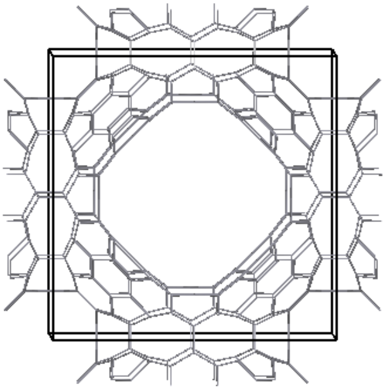
m_opcell2 M_Op_222_ICIF
Diudea,s name diu7



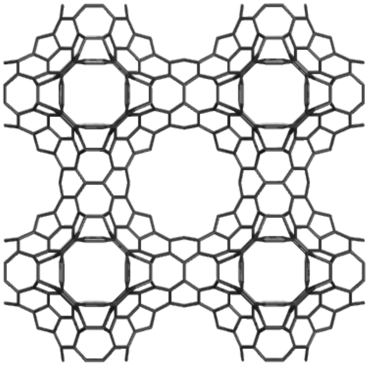
M_Op_222_ICIF
MoZOp

8. NEW (Octahedron, Septupling 2, Leapfrog, normal) diu9=OS2LeN168

Point symbol for net: (5.6.8)2(5.6^2}2(5.8^2)(6.8^2)(6^2.8)2
3,3,3,3,3-c net with stoichiometry (3-c)8; 5-nodal net
VS [6.6.8] [6.8.8] [5.6.8] [5.8.8] [5.6.6]
New topology



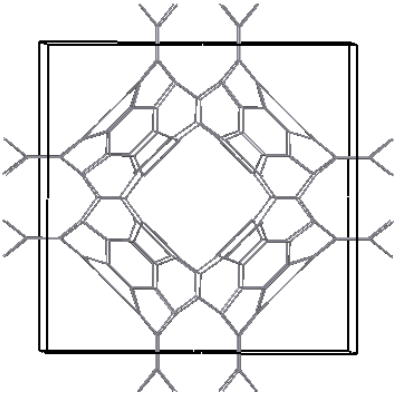
168Ocell 168Oct_S2_Le_N_2x2x2CCC
Diudea,s name diu9



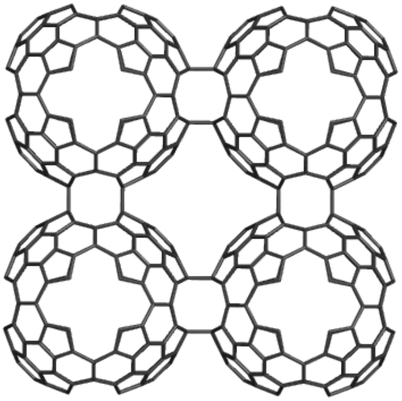
168Oct_S2_Le_N_2x2x2CCC
OS2LeN168

9. NEW (Octahedron, Septupling 2, Leapfrog, Cut edges X) diu10=OS2LeX168

Point symbol for net: (5.10^2)(5.6.9)2(5.6^2)2(6^2.10)
3,3,3,3-c net with stoichiometry (3-c)6; 4-nodal net
VS [5.6.10] [6.6.10] [5.10.10] [5.6.6]
New topology



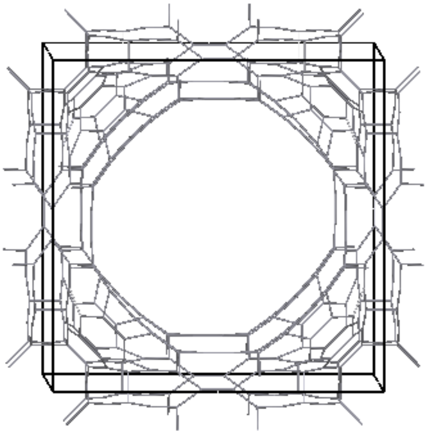
168cell 168Oct_S2_Le_X_222g
Diudea,s name diu10



168Oct_S2_Le_X_222g
OS2LeX168

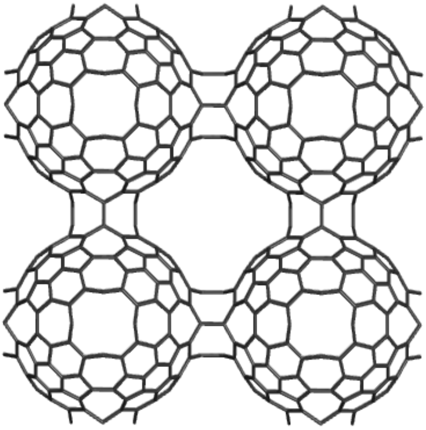
10. NEW (Octahedron, Septupling 2, Leapfrog, Zigzag) diu11=OS2LeZ168

Point symbol for net: $(5.6.7)2(5.6^2)2(5.7^2)(6.7.8)2(7.8^2)$
3,3,3,3,3-c net with stoichiometry (3-c)8; 5-nodal net
VS [5.6.7] [7.8.8] [5.7.7] [5.6.6] [6.7.8]
New topology



168octcell 168Oct_S2_Le_Z_222

Diudea,s name diu11



168Oct_S2_Le_Z_222

OS2LeZ168