ORIGINAL RESEARCH

On diamond D_5

Mircea V. Diudea · Csaba L. Nagy · Attila Bende

Abstract Diamond D_5 is a hyperdiamond structured as coalesced C_{20} and C_{28} small fullerenes, in the ratio 2:1, and having up to 90 % pentagonal rings while the others being hexagonal. Design of several precursors, intermediates, and crystal networks was performed using our original software programs CVNet and Nano-Studio. Energetic data, calculated at DFT and DFTB levels of theory revealed a stability of these structures close to that of classical diamond. A lonsdaleite-like structure is also discussed. The topology of these networks is described in terms of the net parameters and the net characteristics in crystallographic terms.

Keywords Diamond D_5 · Lonsdaleite L_5 · Crystal network · DFT · DFTB · Molecular topology

Introduction

Diamond D_6, the beautiful classical diamond, with all-hexagonal rings of sp^3 carbon atoms (Fig. 1) crystallized in a face-centered cubic network (space group $Fd3m$), has kept its leading interest among the carbon allotropes, even in the nano-era, the period starting in 1985 with the discovery of C_{60} fullerene [1–3]. Its mechanical characteristics are of great importance, as some composites can overpass the resistance and stiffness of steel or other metal

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alloys. Synthetic diamonds can be produced by a variety of methods, including high pressure-high temperature HPHT static or detonation procedures [4–9], chemical vapor deposition CVD [10], ultrasound cavitation [11], or mechano-synthesis [12], under electronic microscopy.

Among the polymorphic diamondoids, structures having a significant amount of sp^3 carbon atoms [13], lonsdaleite [14] is the closest diamond relative [15], with its hexagonal network (space group $P6_3/mmc$, Fig. 2); it was discovered in a meteorite in the Canyon Diablo, Arizona, in 1967 and next synthesized. The evidence of diamond transformation into lonsdaleite was also reported [16].

Multi-tori MT are structures of high genera [1–3], consisting of more than one tubular ring. They are supposed to result by self-assembly of some repeating units (i.e., monomers) which can be designed by opening of cages/fullerenes or by appropriate map/net operations. Multi-tori appear in processes of self-assembling of some rigid monomers [25]. Zeolites [26] and spongy carbon [27, 28], also contain multi-tori. Multi-tori can be designed starting from the Platonic solids, by using appropriate map operations.
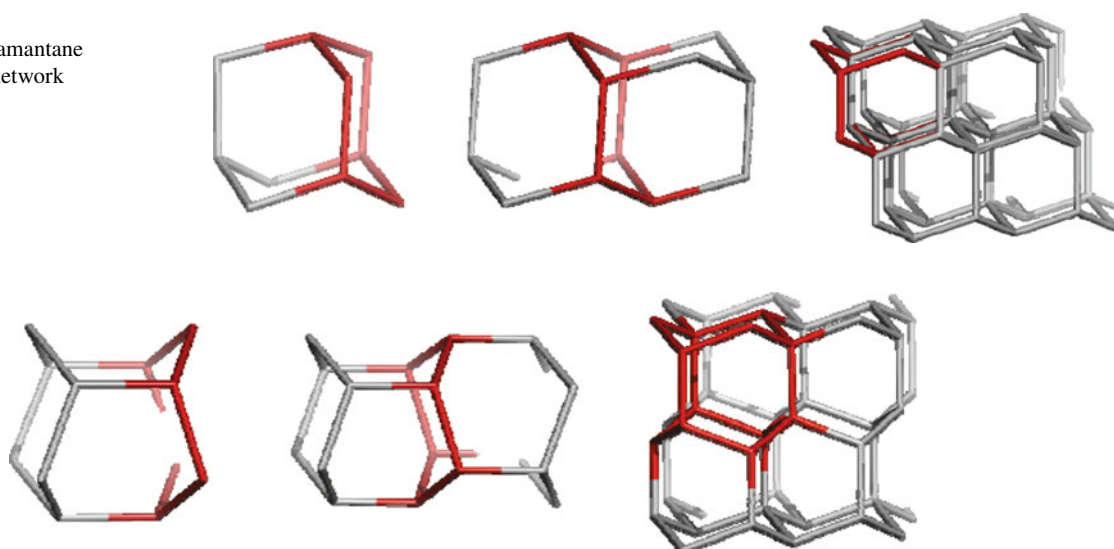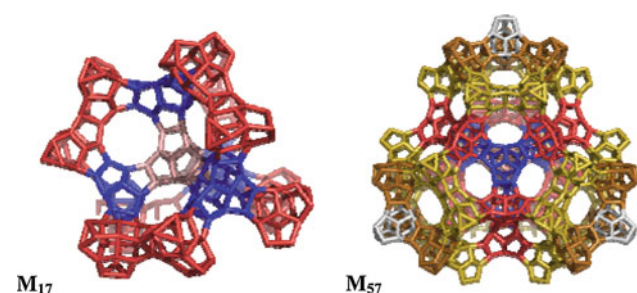
Diamond D_5 network

Diamond D_5, is the name proposed by Diudea [29] for diamondoids consisting mostly of pentagonal rings. Predominance of pentagons over the hexagonal rings is encountered in the spongy diamond SD_5, a periodic structure constructed on the ground of the reduced graphs of multi-torus M_{57} (Fig. 3, right), namely C_{57} (Fig. 4, right), consisting of four C_{20} fullerenes any two such cages sharing a face and all sharing a central point. The central part of C_{57} is the centrohexaquinane skeleton C_{17} (Fig. 4,

Fig. 1 Diamond D_6: adamantane (*left*), diamantane (*middle*) and *Fd*3*m* network (*right*)
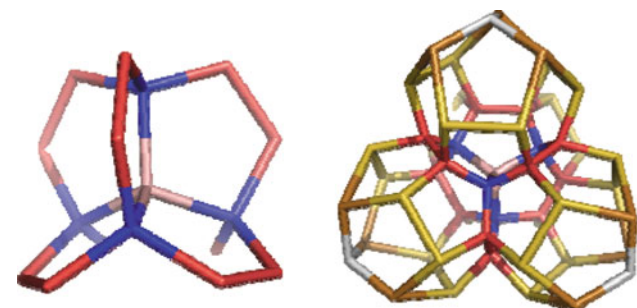

Fig. 2 Lonsdaleite $L_{6\_}$: monomer (*left*), dimer (*middle*) and *P*6₃/*mmc* network (*right*) hyperdiamonds are covalently bonded fullerenes in crystalline forms, more or less related to the diamond D_6 [17]. Several diamond-like networks have also been proposed [2, 18–20]. In a previous study, Diudea and Ilić [21] described some multi-tori
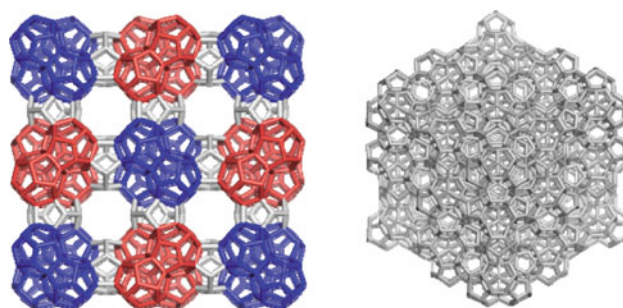
(Fig. 3) constructed by using a unit designed by the map operation [1, 2, 22–24] sequence $Trs(P_4(T))$. These structures consist of all pentagonal faces, observing the triangles disappear (as faces) in the building process

Fig. 3 Multi-tori M_{17} (*left*) and M_{57} (*right*) $v = 972$; $e = 1770$; $f_5 = 684$

left), which is the reduced graph of multi-torus M_{17} (Fig. 3, left).

The nodes of diamond SD_5 network (Fig. 5) consist of C_{57} units and the network is a triple periodic one. The number of atoms, bonds, and C57 monomers m, as well as

the number of pentagons R [5] and the content in sp^3 carbon C (deg 4), given as a function of k—the number of monomers along the edge of a (k,k,k) cuboid. At limit, in an infinite net, the content of sp^3 carbon approaches 77 % (Table 1).

Crystallography of SD_5 is as follows: the net is a 7-nodal net, with cubic symmetry *Fm*-3*m*, its point symbol being {5^3}16{5^5.8}36{5^6}17 3,3,4,4,4,4,4-c, with the stoichiometry (3-c)4(3-c)12(4-c)4(4-c)12(4-c)24(4-c)12(4-c).

C_{17} (Fig. 4, left) is supposed to dimerize, as centrohexaquinacene, by a synchron cycloaddition, to $2 \times C_{17} = C_{34}$ (Fig. 6, right), which is the repeating unit of dense diamond D_5 [30].

This dominant pentagon-ring diamond (Fig. 7, see also Table 3) is a *mtn* triple periodic, 3-nodal net, namely ZSM-39, type II clathrate, of point symbol net: {5^5.6}12{5^6}5 and $2[5^{12}] + [5^{12} \times 6^4]$ tiling and belongs to the space

Fig. 4 The centrohexaquinane C_{17} (*left*) and the multi-cage C_{57}: $v = 57$; $e = 94$; $r_5 = 42$ (*right*)

Fig. 5 SD₅ (C_{57} based) triple periodic network: top view (*left*) and corner view (*right*)
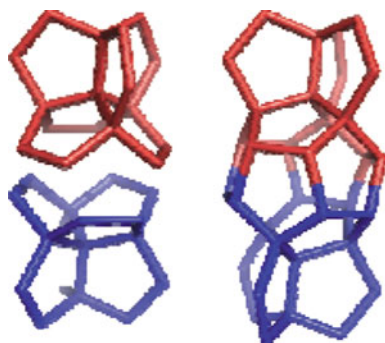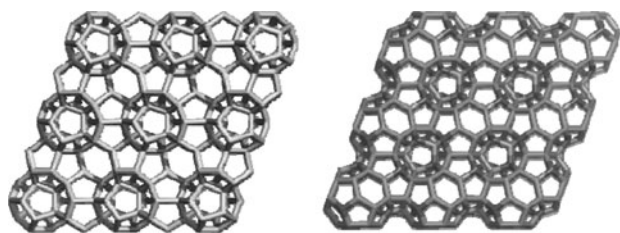
Table 1 Topology of the spongy SD5, a C_{57}-based net

	Formulas
1	Atoms($SD_5 \_ 57$) = $k (69 k - 12)$
2	Bonds($SD_5 \_ 57$) = $2 k (65 k - 18)$
3	$m(SD_5 \_ 57) = k^3$; $m = 57\_unit$; $k = 1, 2, \cdots$
4	$C(\deg 3) = 8 k^2 (2 k + 3)$
5	$C(\deg 4) = k^2 (53 k - 36)$
6	$R[5] = 6 k^2 (11 k - 4)$
7	$\lim \dfrac{C(°4)}{\text{Atoms}(SD_5\_57)} = 53/69 = 0.768116$

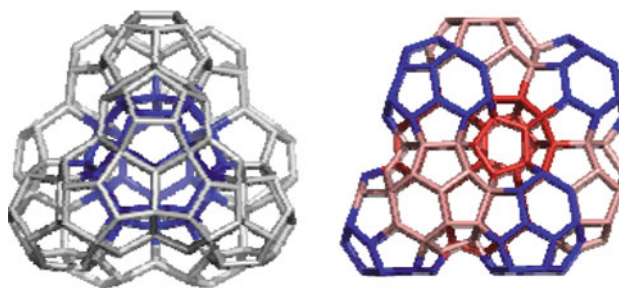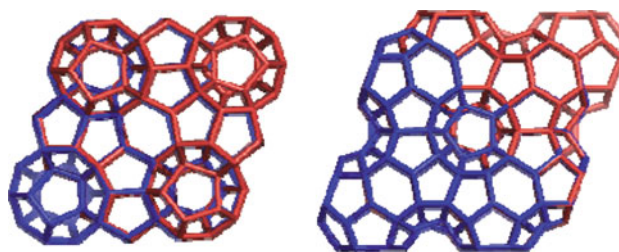group: $Fd3m$. It is also known as fcc C_{34} structure, because of its face-centered cubic lattice.

In words, the network of D_5 consists of C_{20} (i.e., dodecahedron, a 12-hedron) and C_{28} (i.e., hexakaidecahedron, a 16-hedron) fullerene cages, in ratio 2:1; each edge shares three cages and each carbon atom shares four cages. Looking from C_{28} fullerene, the co-net is like that in Fig. 7, right. The name of structures, hereafter, includes the type of net, number of cage atoms and the total number of atoms/points in the net.

Recall that clathrates represent foamy structures, like crystals of ice or some metal alloys [30–39]. They have been introduced in the late 40th to describe crystal structures with organic inclusions or chlorine hydrate structures or also pure carbon clathrate structures [32, 35–37]. An infinite fullerenic clathrate lattice is a polyhedral filling of the 3D space resulting by the coalescence of fullerenic

cages, so that all atoms are of fourfold connected, with eclipsed sp^3 bonding, to their neighbors, and form exclusively five- or six-membered rings [35].

In a chemist view, the building of D_5 network may start with the seed C_{17} structure and continue with modeling of some intermediates, the adamantane- and diamantane-like ones included (Figs. 8, 9, and 10). The structure ada_20_158 (Fig. 9, left), corresponds to adamantane (Fig. 1, left) in the classical diamond D_6. The ada-like structure, starting from C_{28} can be seen in Fig. 9, right). Diamantane-like units can also be modeled, as in Fig. 10 (see for comparison the diamantane, Fig. 1, middle). In fact, there is one and the same *triple periodic* D_5 network, built up basically from C_{20} and having as hollows the fullerene C_{28}. The co-net D_5_28 cannot be derived from C_{28} alone since the hollows of such a net consist of C_{57}
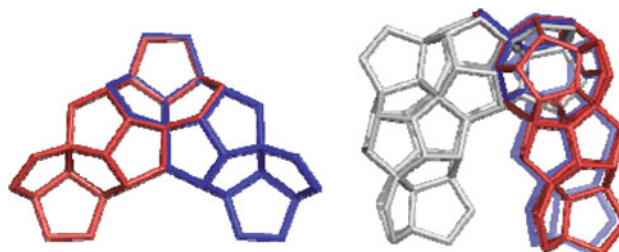
Fig. 8 Intermediate structures originating in C_{34} unit: C_{51} (*left*) and $3 \times C_{51}$ (*right*)

Fig. 6 Dimerization of C_{17} (*left*) to C_{34} (*right*)—the repeating unit of dense diamond D_5

Fig. 9 Adamantane-like structures: ada_20_158 (*left*) and ada_28_213 (*right*)

Fig. 7 Diamond $D_5\_20\_860$ net (*left*) and $D_5\_28\_1022$ co-net (*right*)

Fig. 10 Diamantane-like structures: dia_20_226 net (*left*) and dia_28_292 co-net (*right*)

units (a C_{20}-based structure, see above) or higher tetrahedral arrays of C_{20} thus needing extra C atoms per ada-unit.

It is worthy to note the stabilizing effect of the wings in case of C_{34} (Fig. 6, right) in comparison to C_{20}. Remark the efforts made by a series of bright scientists [40–44] to reach the dodecahedral cage C_{20}, either as fullerene or hydrogenated species. Also remark the endeavor to synthesize the centrohexaquinane C_{17}, both as oxygen-containing heterocycle [45, 46] or all carbon structure [47, 48].

Thus, the hyperdiamond D_5_20/28 mainly consists of sp^3 carbon atoms building adatype repeating units (including C_{28} as hollows). The ratio C-sp^3/C-total trends to 1 in a large enough network. As the content of pentagons R [5] per total rings trend to 90 %, this, network was named the diamond D_5.

Table 2 B3LYP/6-31G(d,p) single point energy results

	Formula	Symmetry	GAP (eV)	E_{tot}/N (a.u.)
1	$C_{10}H_{16}$	T_d	9.32	−39.08
2	C_{20}	D_{2h}	1.94	−38.07
3	C_{60}	I_h	2.76	−38.10
4	C_{57}	D_{2d}	1.89	−38.53
5	$C_{20}H_{20}$	I_h	8.00	−38.71
6	$C_{57}H_{40}$	T_d	7.37	−38.08
7	$C_{17}H_{12}$	T_d	6.04	−38.27
8	$C_{34}H_{12}$	D_{3d}	3.24	−38.31
9	$C_{158}H_{12}(D_5$_20)	T_d	3.25	−38.14
10	$C_{213}H_{28}(D_5$_28)	T_d	3.70	−38.18
11	$C_{134}H_{20}$ (L_5_28)	D_{3d}	3.74	−38.19
12	$C_{250}H_{30}$ (L_5_28)	D_{3h}	0.33	−38.17

Lonsdaleite L5 network

A lonsdaleite-like net was also proposed (Fig. 11). It consist of hyper-hexagons L_5_28_134 (Fig. 11, central and right), of which nodes represent the C_{28} fullerene, was used as the monomer (in the chair conformation). The corresponding L_5_20 co-net was also designed. The lonsdaleite L_5_28/20 is partially superimposed on D_5_20/28 net. In crystallographic terms, lonsdaleite L_5 represents the *mgz-x-d* net, with the point symbol: {5^5.6}12{5^5.6}5; 4,4,4,4,4,4,4-c, and is a 7-nodal net.

Design of several hypothetical crystal networks was performed by using our original software programs CVNet [49] and Nano Studio [50]. Topological data were provided by the Nano Studio program.

Theoretical calculations

Energetic data, calculated at the hybrid B3LYP density functional level of theory using the standard polarized 6-31G(d,p) basis set show a good stability of the start and intermediate structures (single point energy results are summarized in Table 2). Geometry optimizations with and without symmetry constraints resulted in identical structures. All the calculations were performed using the Gaussian 09 package [51].

Partially hydrogenated molecular fragments of the hyperdiamond and hyperlonsdaleite networks have been evaluated for stability, data proving a pertinent stability of the D_5 diamond. The energy of the precursors ranges between that of the adamantine $C_{10}H_{16}$–T_d and the C_{60}–I_h fullerene, taken as reference structures (see Table 2).

Due to the huge number of atomic components, the large carbon networks could not be properly described in the framework of the ab initio or the conventional DFT molecular theories. In contrast, the density functional-based tight-binding method combined with the selfconsistent charge technique (SCC–DFTB) [52] can be considered as an adequate solution for treating large biologically interested or nanoscaled molecular materials with nearly good accuracy as obtained in the case of high-level theoretical methods [53–55].

The carbon network structure of Diamond D_5_20_860 net and D_5_28_1022 co-net (see Fig. 7) were optimized using the DFTB + program [56, 57] considering the numerical conjugated gradient method. Hydrogen atoms were added to the external carbon atoms of the network structures, in order to keep the charge neutrality and the sp^3 character of the C–C bonds at the network surface. In both cases, energetically stable geometry structures were obtained, where the repeating unit of dense diamond D_5 is kept.

Fig. 11 Lonsdaleite: L_5_28_250 (*side view*, *left*), and its consisting hyper-hexagon L_5_28_134 (*side and top view*, *central*, and *right*, respectively)
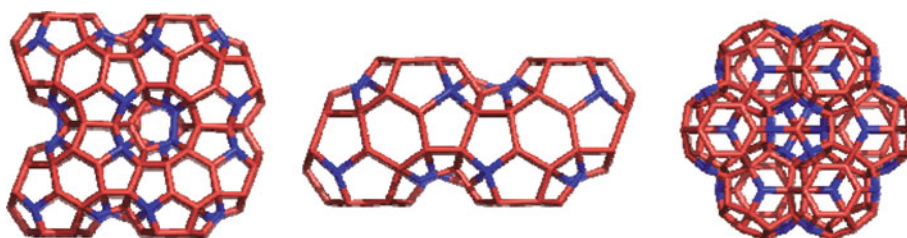
Identification of the equivalent carbon atoms in the neighboring units of the $3 \times 3 \times 3$ super-cell along the main symmetry axes, envisaged a well-defined triclinic lattice, with the following parameters: $a = b = c = 6.79$ Å, as well as, $\alpha = 60°$, $\beta = 120°$, $\gamma = 120°$, even the most symmetrical structure is fcc-one [30]. Density of the D5 network was calculated to be around 2.8 g/cm^3.

Analyzing the C–C bond distances in these carbon networks, these values vary in a very narrow distance domain of 1.50–1.58 Å, showing that all C–C bonds present sp^3 valence orbital hybridization. Considering the one-electron energy levels of the HOMO and LUMO, a very large energy gap can be observed for both D$_5$_20_860 net ($E_{HOMO} = -5.96$ eV, $E_{LUMO} = +2.10$ eV, $\Delta E_{HOMO-LUMO} = 8.06$ eV) and D$_5$_28_1022 co-net ($E_{HOMO} = -6.06$ eV, $E_{LUMO} = +2.45$ eV, $\Delta E_{HOMO-LUMO} = 8.51$ eV) structures, which indicates an insulating behavior for this carbon network, similar to the classical diamond D$_6$ [35, 39, 58].

Topology of diamond D$_5$

Topology of diamond D$_5$, in a (k,k,k) cuboid (see Fig. 7), is presented in Table 3 and Table 4: formulas to calculate the number of atoms, number of rings, and the limits (at infinity) for the ratio of sp^3 C atoms over the total number of atoms and also the ratio R [5] over the total number of rings are given function of k. The network parameters are: $a = b = c = 6.79$ Å, while the angles between axes are 60, 120, and 120°, respectively.

Conclusions

Diamond D$_5$ is a hyperdiamond structured on the type II clathrate network, also known as fcc-C$_{34}$. Design of several precursors, intermediates, and crystal networks was performed using our original software programs CVNet and Nano-Studio developed at TOPO GROUP CLUJ. Energetic

Table 3 Omega polynomial in Diamond D$_5$_20 net function of $k = 1, 2, \cdots$ no. of ada_20 units along the edge of a (k,k,k) cuboid

	Formulas
1	$v(D_5\_20a) = -22 - 12\,k + 34\,k^3$
2	$\text{Atoms}(sp^3) = -10 - 36\,k^2 + 34\,k^3$
3	$R[5] = -18 - 6\,k - 18\,k^2 + 36\,k^3$
4	$R[6] = -1 + 6\,k - 9\,k^2 + 4\,k^3$
5	$R[5] + R[6] = -19 - 27\,k^2 + 40\,k^3$
6	$\lim_{k\to\infty} \frac{R[5]}{R[6]} = 9$; $\lim_{k\to\infty} \frac{R[5]}{R[5]+R[6]} = 9/10$
7	$\lim_{k\to\infty}\left[\frac{\text{Atoms}(sp^3)}{v(G)} = \frac{-10-36k^2+34k^3}{-22-12k+34k^3} = \frac{-\frac{10}{k^3}-\frac{36}{k}+34}{-\frac{22}{k^3}-\frac{12}{k^2}+34}\right] = 1$

Table 4 Omega polynomial in D$_5$_28 co-net function of $k =$ no. ada_20 units along the edge of a (k,k,k) cuboid

	Omega (D$_5$_28a); R[6]; formulas
1	$v(D_5\_28a) = -40 - 6\,k + 18\,k^2 + 34\,k^3$
2	$\text{Atoms}(sp^3) = -4 - 6\,k - 30\,k^2 + 34\,k^3$
3	$R[5] = -18 - 18\,k^2 + 36\,k^3$
4	$R[6] = -1 + 6\,k - 9\,k^2 + 4\,k^3$
5	$\lim_{k\to\infty}\left[\frac{\text{Atoms}(sp^3)}{v(G)} = \frac{-4-6k-30k^2+34k^3}{-40-6k+18k^2+34k^3}\right] = 1$

data, calculated at DFT and DFTB levels of theory, revealed a stability of these structures close to that of classical diamond and its units. A lonsdaleite-like network is also discussed. The topology of these structures is described in terms of the net parameters and the net characteristics in crystallographic terms.

References

1. Diudea MV (2010) Nanomolecules and nanostructures: polynomials and indices. Univ, Kragujevac
2. Diudea MV, Nagy CL (2007) Periodic nanostructures. Springer, Dordrecht
3. Nagy CL, Diudea MV (2005) In: Diudea MV (ed) Nanostructures, novel architecture. NOVA, New York
4. Aleksenskiĭ AE, Baĭdakova MV, Vul AY, Davydov VY, Pevtsova YA (1997) Diamondgraphite phase transition in ultradisperse-diamond clusters. Phys Solid State 39:1007–1015
5. Williams OA, Douhéret O, Daenen M, Haenen K, Osawa E, Takahashi M (2007) Enhanced diamond nucleation on monodispersed nanocrystalline diamond. Chem Phys Lett 445:255–258
6. Decarli PS, Jamieson JC (1961) Formation of diamond by explosive shock. Science 133:1821–1822
7. Osawa E (2008) Monodisperse single nanodiamond particulates. Pure Appl Chem 80:1365–1379
8. Osawa E (2007) Recent progress and perspectives in single-digit nanodiamond. Diam Relat Mater 16:2018–2022
9. Dubrovinskaia N, Dub S, Dubrovinsky L (2006) Superior wear resistance of aggregated diamond nanorods. Nano Lett 6:824–826
10. Lorenz HP (1995) Investigation of TiN as an interlayer for diamond deposition on steel. Diam Relat Mater 4:1088–1092
11. Khachatryan AK, Aloyan SG, May PW, Sargsyan R, Khachatryan VA, Baghdasaryan VS (2008) Graphite-to-diamond transformation induced by ultrasound cavitation. Diam Relat Mater 17:931–936
12. Tarasov D, Izotova E, Alisheva D, Akberova N, Freitas RA Jr (2011) Structural stability of clean, passivated, and partially dehydrogenated cuboid and octahedral nanodiamonds up to 2 nanometers in size. J Comput Theor Nanosci 8:147–167
13. Robertson J (2002) Diamond-like amorphous carbon. Mater Sci Eng R 37:129–281

14. Frondel C, Marvin UB (1967) Lonsdaleite, a hexagonal polymorph of diamond. Nature 214:587–589
15. Balaban AT, Ragé Schleyer PV (1978) Systematic classification and nomenclature of diamond hydrocarbons-I. Graph-theoretical enumeration of polymantanes. Tetrahedron 34:3599–3609
16. He H, Sekine T, Kobayashi T (2002) Direct transformation of cubic diamond to hexagonal diamond. Appl Phys Lett 81:610–612
17. Ivanovskii AL (2008) Hyperdiamonds. Russ J Inorg Chem 53:1274–1282
18. Sunada T (2008) Crystals that nature might miss creating. Notices Am Math Soc 55:208–215
19. Diudea MV, Bende A, Janežič D (2010) Omega polynomial in diamond-like networks. Fuller Nanotub Carbon Nanostruct 18:236–243
20. Hyde ST, O'Keeffe M, Proserpio DM (2008) A short history of an elusive yet ubiquitous structure in chemistry, materials, and mathematics. Angew Chem Int Ed 47:7996–8000
21. Diudea MV, Ilić A (2011) All-pentagonal face multi tori. J Comput Theor Nanosci 8:736–739
22. Diudea MV (2004) Covering forms in nanostructures. Forma (Tokyo) 19:131–163
23. Diudea MV, Stefu M, John PE, Graovacc A (2006) Generalized operations on maps. Croat Chem Acta 79:355–362
24. Diudea MV (2005) Nanoporous carbon allotropes by septupling map operations. J Chem Inf Model 45:1002–1009
25. Diudea MV, Petitjean M (2008) Symmetry in multi tori. Symmetry Cult Sci 19:285–305
26. Anurova NA, Blatov VA, Ilyushin GD, Proserpio DM (2010) Natural tilings for zeolite-type frameworks. J Phys Chem C 114:10160–10170
27. Benedek G, Vahedi-Tafreshi H, Barborini E, Piseri P, Milani P, Ducati C, Robertson J (2003) The structure of negatively curved spongy carbon. Diam Relat Mater 12:768–773
28. Barborini E, Piseri P, Milani P, Benedek G, Ducati C, Robertson J (2002) Negatively curved spongy carbon. Appl Phys Lett 81:3359–3361
29. Diudea MV (2010) Diamond D_5, a novel allotrope of carbon. Studia Univ Babes-Bolyai Chemia 55:11–17
30. Benedek G, Colombo L (1996) Hollow diamonds from fullerenes. Mater Sci Forum 232:247–274
31. Delgado-Friedrichs O, O'Keeffe M (2006) On a simple tiling of Deza and Shtogrin. Acta Crystallogr A 62:228–229
32. Aste T, Weaire D (2008) The pursuit of perfect packing. Taylor and Francis, Bristol
33. Delgado-Friedrichs O, O'Keeffe M (2010) Simple tilings by polyhedra with five- and sixsided faces. Acta Crystallogr A 66:637–639
34. Sikirić MD, Delgado-Friedrichs O, Deza M (2010) Space fullerenes: a computer search for new Frank–Kasper structures. Acta Crystallogr A 66:602–615
35. Blase X, Benedek G, Bernasconi M (2010) In: Colombo L, Fasolino A (eds) Computer-based modeling of novel carbon systems and their properties beyond nanotubes. Springer, New York
36. Pauling L, Marsh RE (1952) The structure of chlorine hydrate. Proc Natl Acad Sci USA 38:112–118
37. Powell HM (1948) The structure of molecular compounds. Part IV. Clathrate compounds. J Chem Soc 1:61–72
38. Delgado-Friedrichs O, O'Keeffe M, Yaghi OM (2006) Three-periodic nets and tilings: edge-transitive binodal structures. Acta Crystallogr A 62:350–355
39. Adams GB, Okeeffe M, Demkov AA, Sankey OF, Huang YM (1994) Wide-band-gap Si in open fourfold-coordinated clathrate structures. Phys Rev B 49:8048–8053
40. Prinzbach H, Wahl F, Weiler A, Landenberger P, Wörth J, Scott LT, Gelmont M, Olevano D, Sommer F, Von Issendorff B (2006) C_{20} carbon clusters: fullerene-boat-sheet generation, mass selection, photoelectron characterization. Chem Eur J 12:6268–6280

41. Paquette LA, Balogh DW, Usha R, Kountz D, Christoph GG (1981) Crystal and molecular structure of a pentagonal dodecahedrane. Science 211:575–576
42. Prinzbach H, Weller A, Landenberger P, Wahl F, Wörth J, Scott LT, Gelmont M, Olevano D, Issendorff BV (2000) Gas-phase production and photoelectron spectroscopy of the smallest fullerene, C_{20}. Nature 407:60–63
43. Saito M, Miyamoto Y (2001) Theoretical identification of the smallest fullerene, C_{20}. Phys Rev Lett 87:355031–355034
44. Eaton PE (1979) Towards dodecahedrane. Tetrahedron 35:2189–2223
45. Simmons Iii HE, Maggio JE (1981) Synthesis of the first topologically non-planar molecule. Tetrahedron Lett 22:287–290
46. Paquette LA, Vazeux M (1981) Threefold transannular epoxide cyclization. Synthesis of a heterocyclic C_{17}-hexaquinane. Tetrahedron Lett 22:291–294
47. Gestmann D, Pritzkow H, Kuck D (1996) Partially benzoanellated centrohexaquinanes: oxidative degradation of centropolyindanes by using ruthenium(VIII) oxide and ozone. Liebigs Ann 9:1349–1359
48. Kuck D (2006) Three-dimensional hydrocarbon cores based on multiply fused cyclopentane and indane units: centropolyindanes. Chem Rev 106:4885–4925
49. Stefu M, Diudea MV (2005) CageVersatile CVNet. Babes-Bolyai University, Cluj-Napoca
50. Nagy CL, Diudea MV (2010) Nano studio. Babes-Bolyai University, Cluj-Napoca
51. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, J. A. Montgomery J, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Revision A.02. Gaussian Inc., Wallingford
52. Elstner M, Porezag D, Jungnickel G, Elsner J, Haugk M, Frauenheim T, Suhai S, Seifert G (1998) Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties. Phys Rev B 58:7260–7268
53. Elstner M, Jalkanen KJ, Knapp-Mohammady M, Frauenheim T, Suhai S (2000) DFT studies on helix formation in N-acetyl-(L-alanyl)(n)-N'-methylamide for $n = 1–20$. Chem Phys 256:15–27
54. Elstner M, Jalkanen KJ, Knapp-Mohammady M, Frauenheim T, Suhai S (2001) Energetics and structure of glycine and alanine based model peptides: approximate SCC–DFTB, AM1 and PM3 methods in comparison with DFT, HF and MP2 calculations. Chem Phys 263:203–219
55. Elstner M, Hobza P, Frauenheim T, Suhai S, Kaxiras E (2001) Hydrogen bonding and stacking interactions of nucleic acid base pairs: a density functional-theory based treatment. J Chem Phys 114:5149–5155
56. DFTB+ 1.1 is a DFTB implementation, which is free for non-commercial use. For details, see: http://www.dftbplus.info
57. Aradi B, Hourahine B, Frauenheim T (2007) DFTB+, a sparse matrix-based implementation of the DFTB method. J Phys Chem A 111:5678–5684
58. Nesper R, Vogel K, Blöchl PE (1993) Hypothetical carbon modifications derived from zeolite frameworks. Angew Chem Int Ed 32:701–703