Is the Clathrate Diamond Possible?

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Abstract

Topological analysis of real and possible crystal modifications of carbon is performed. At present, a series of condensed carbon forms in sp^2-coordination is obtained. Some versions of the topology of hypothetical crystal modifications of sp^2 carbon are considered. Only two crystal modifications of sp^3 carbon have been realized by present. They are: cubic and hexagonal diamond. A hypothesis is put forward concerning the possibility for new sp^3-coordinated crystal carbon modifications to exist, their regular space grid being formed by polyhedra with cubic vertexes packed so that they fill the space completely. These structures occur in clathrate hydrates, clatrasiles and clathrate compounds of carbon analogs (silicon, germanium, and tin). One of the possible clathrate structures is calculated and its energy is estimated using harmonic potential.

INTRODUCTION

The development of the chemistry of carbon compounds cannot be considered without the forecast of new molecular structures and unusual carbon frameworks that can become the basis of new classes of organic compounds. In the present study we prove the possibility for structures composed of carbon atoms to exist, and the place is determined which is occupied by these structures in topological classification of crystal polymorphous modifications of this element. Lattices of these structures are composed of polyhedra packed regularly and filling up the space. Because of this, we consider polyhedral carbon clusters in brief, then analyse topological principles according to which the crystal modifications of carbon are built, and describe structural analogies of hypothetical carbon structures considered by us. To conclude, we present the calculation of the lattice parameters for one of these structures and estimation of the energy of its formation from diamond.

POLYHEDRAL CARBON CLUSTERS

Within the frames of the present study, it is reasonable to follow in brief the history of the discovery of convex polyhedron-shaped carbon clusters. If sp^3-coordinated carbon atoms are in their vertexes, three bonds of each atom are directed along the edges of polyhedron while the fourth one is involved in binding the ligand. Polyhedra built of sp^2 atoms are carbon molecules. So, both kinds of carbon atoms can form only polyhedra with cubic vertexes. According to [1], we shall designate these polyhedra as $A^a B^b \dots$ Polyhedron meeting this condition has faces containing A, B, … edges, the number of such faces being a, b, …

The first example of the forecast of carbon polyhedron can be the structural interpretation of benzene formula by Ladenburg in 1847. He assumed that carbon atoms are situated in the vertexes of triangular prism $3^2 4^3$ (Fig. 1) belonging to the group of semiregular polyhedra (Archimedean bodies). Organic compounds with such a framework were synthesized only in the early 70ies [2]. Researchers in chemistry
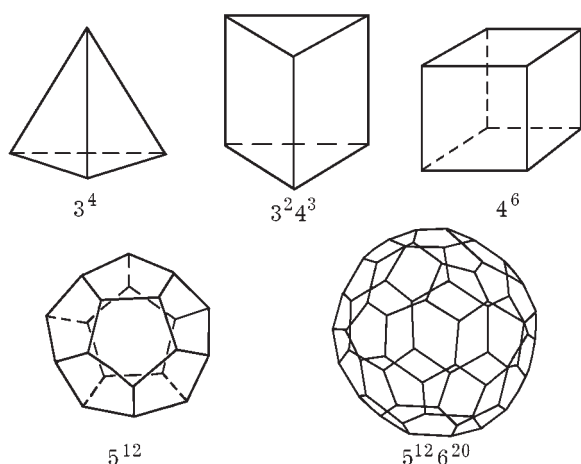
Fig. 1. Polyhedral frameworks composed of carbon atoms and arranged as regular and semiregular polyhedrons.

are aesthetically interested in atomic structures shaped as regular polyhedra among which only three (namely, tetrahedron 3^4, cube 4^6 and pentagonal dodecahedron 5^{12}) have only the 3rd-order vertexes. Unsubstituted cubane was synthesized in 1964 [3]. The calculation of the molecule $C_{20}H_{20}$ performed in 1965 [4] showed high thermal stability of this hydrocarbon. The attempts to synthesize the compounds with such a framework took a long period of time but only in 1982 this goal was achieved [5]. At present, the chemistry of dodecahedrane is extensively developing. The possibility to synthesize a very stressed tetrahedrane structure was discussed many times [6]. The derivatives of this compound have been synthesized. However, the most widely known forecast in carbon chemistry was connected with the discovery of fullerenes. The stability of carbon structure C_{60} as an Archimedean polyhedron $5^{12}6^{20}$ was demonstrated with the help of quantum chemical calculations carried out by Ozawa (1970), Bochvar and Galperin (1973), *etc.* [7, 8]. However, experimenters ignored these studies. After species with molecular mass corresponding to C_{60} were discovered in carbon vapour, their structure was to be invented once more.

**TOPOLOGICAL CLASSIFICATION
OF CRYSTAL CARBON MODIFICATIONS**

The above-mentioned examples suggest that the forecasts of new carbon structures can be promising. The discovery of fullerenes

[9] and nanotubulenes [10] demonstrated extremely wide possibilities for the formation of various structures composed of carbon atoms. Modelling of the topology of these structures and the forecast of their properties are among the most important means to research these specific chemicals. However, it can hardly be assumed that structural possibilities of carbon have been investigated completely. Where can principally new carbon structures be searched for? What class of allotropic modifications may these hypothetical structures belong to?

If we exclude unsaturated carbon species C, C_2, *etc.* when considering vapour, three groups of allotropic carbon modifications can be revealed. They are composed of sp-, sp^2- and sp^3-coordinated atoms. In the condensed phase the corresponding polymorphous modifications are carbine, graphite and diamond groups (Fig. 2). All of them are able to exist as topologically different spatial structures including crystal ones.

Unidimensional crystals can be formed by packing chain molecules of carbine or nanotubulenes, carbon tubes with the walls formed by wrapped band which is a graphite layer. These tubes differ both in diameter and in the features of graphite rings packing (in circle or in spiral with some spacing). Besides, multilayered nanotubulenes are known [11]. Because of this, one can expect that there are varieties of crystal modifications of nanotubulenes formed by packing of carbon tubes, either similar or differing in size and configurations. The substitution of a part of hexagons in the tubes with pentagons and heptagons leads to surface curvature in two directions or to the formation of conical surface. If six pentagons are introduced into the graphite plane, a hemisphere is formed. It can serve as the end of carbon tube. So, the possibility arises for the formation of tubes closed from one end or both. Because of this, the number of possible structures of nanotubulene crystals increases.

If 12 pentagons are inserted into graphite layer, we obtain a closed spheroid. Its size depends on the number of hexagonal cycles. The most stable molecule is a spherical C_{60}. The fullerenes C_{70}, C_{76}, C_{84}, C_{90}, C_{94} have also been isolated as individual practically pure species [7]. Due to the existence of fullerene molecules with

C

sp (carbine group) ——————————————— One-dimensional crystal structures

sp^2 (graphite group)

Nanotubulenes

Graphite

    Hexagonal
    Rhombic — Two-dimensional crystal structures
    Polytypes

Fullerenes

    C_{60} — Zero-dimensional crystal structures
    C_{70}

sp^3 (diamond group)

Diamond

    Cubic
    Hexagonal
    Polytypes

Polyhedral structures — Three-dimensional crystal structures
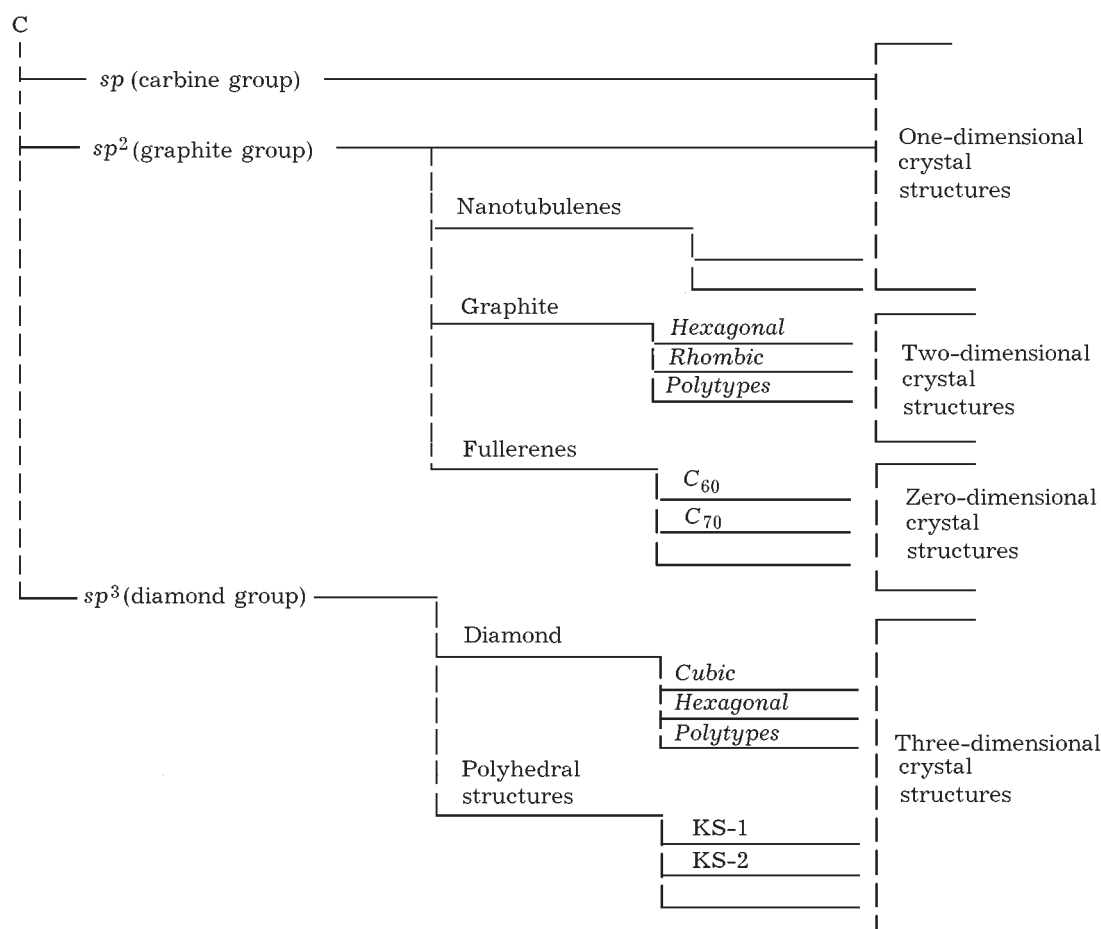
    KS-1
    KS-2

Fig. 2. Crystal polymorphous modifications of carbon (existing and hypothetical ones).

magic numbers of carbon atoms (including the "bulbous structures"), the possibility arises to build up lattices (fullerites) composed of identical molecules. For example, the fullerites are obtained that are composed from C_{60} and C_{70} molecules [7]. One also cannot exclude the possibility for mixed crystals to be formed from two or more kinds of fullerene molecules. These crystals can be considered as solid solutions of carbon in carbon.

There are two simplest topological versions of the packing of hexagonal nets into a two-dimensional crystal. They are realized in the hexagonal and rhombic graphite [12]. More complicated topologies are connected with the possibility of the existence of polytypes formed by these two versions of layer packing.

An important property of graphite is its ability to allow intercalation of guest atoms and molecules between the carbon planes [13]. A similar property is also exhibited by nanotubulenes [14]. This circumstance allows us to imagine purely carbon intercalates when the role of guest molecules in graphite or nanotubulene is played by fullerene molecules. To estimate the possibility of these structures, special analysis is necessary.

TETRAHEDRAL CARBON FRAMEWORKES

The review presented above indicates that the topological possibilities of structures composed of sp^3-coordinated carbon atoms are extremely broad. At present diamond and lonsdaylite are known as crystal structures composed of sp^3-coordinated atoms [12]. Are other carbon structures of this class possible? If yes, then how diverse can they be? To answer these questions, it is necessary first of all to analyse the topology of spatial frameworks in which the length of edges is close to the length of unstressed C—C bond and C—C—C angles are rather close to tetrahedral ones.
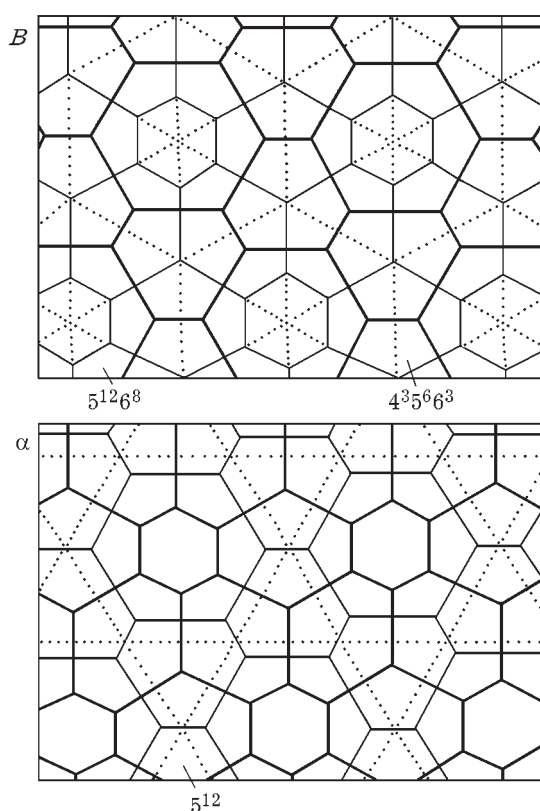
Fig. 3. A scheme of the lattice of clathrate framework with HS-3.

Besides the cubic and hexagonal diamond structures, there are many regular tetrahedral frameworks of lower density. Among them, most interesting are the frameworks built of tetrahedrally coordinated atoms or molecules that occur in the structures of chemical compounds. These frameworks are packed polyhedra with cubic vertexes filling the space up completely. Polyhedral lattices built of tetrahedral particles are typical of clathrate compounds. The most widely known among them are clathrate hydrates [15]. Empty polyhedral lattices composed of water molecules that may be considered as low-density ice phases are metastable. Guest molecules are inside the polyhedra thus stabilizing the framework. As a result, stable hydrate is formed. By present, gas hydrates of more than 120 volatile low-molecular compounds have been obtained. Nearly all of them possess cubic structures CS-1 and CS-2 [16]. The properties of these frameworks are studied extensively by means of modelling [17, 18]. The formation of water frameworks from ice I_h in clathrate hydrates leads to the deformation of both the bond lengths and an-

gles. The major contribution into the energy of phase transition from clathrate framework to ice is made by the angular constituent [19]. This circumstance poses limitations on possible kinds of polyhedral faces. Inner angles in pentagons are only slightly different from the tetrahedral angle; the next in angular stress are hexagons. Because of this, the preferable structural elements of water frameworks in clathrate and semiclathrate hydrates are polyhedra faced by penta- and hexagons. The compounds with these frameworks are most widespread [20] while water frameworks with tetra- and heptagon cycles are rare [21]. A correlation is observed between the energy of framework formation and the number of different cycles in the unit cell [22].

Structurally similar frameworks composed of SiO_2 are present in clathrasiles [23−25]. But especially interesting is the existence of clathrate compounds with the frameworks formed by the atoms of carbon analogs − silicon, germanium, and tin [26, 27]. The lattices of these compounds include cubic frameworks CS-1 and CS-2. The atoms of alkaline metals are inside their voids. The atoms in frameworks are bound by covalent bonds. Crystals exhibit metal-type conductivity which means that the guest sub-lattice can be considered as low-density metal phase.

Crystal structures of diamond, germanium, silicon and grey tin are similar. It can be expected that the similarity exists also for polyhedral frameworks [28]. The existence of these frameworks composed of the atoms of elements analogous to carbon allows one to assume the existence of polyhedral frameworks built of carbon atoms coordinated as tetrahedrons. The properties of these frameworks should be similar to those of diamond, so it is convenient to call these frameworks "clathrate diamonds".

Empty frameworks are characterized by higher energy than diamond-like lattices, that is why the former are metastable. However, the existence of metastable compounds is characteristic of carbon chemistry which is due to high C—C bond energy and high potential barriers for the rearrangement of carbon frameworkes. Because of this, metastable polyhedral carbon frameworks may be expected to be stable under usual conditions.

Topological properties of these frameworks were considered in [29, 30]. An infinite number of polyhedral frameworks built of tetrahedral particles exists. However, most attractive among them are those with minimal formation energy. As in clathrate hydrates, the energy of formation of the polyhedral lattices composed of carbon atoms is determined mainly by distortions of valence angles. Therefore, for carbon, similarly to water, the less strained frameworks should possess the CS-1 and CS-2. The calculations of structure and estimations of the energy of these frameworks are presented in [28] with the help of power constants for the C—C bond vibrations and the deformation of the C—C—C valence angle taken from [31]. Estimated energy of the formation of clathrate framework from diamond is 22.15 and 16.27 kJ/mole for CS-1 and CS-2, respectively. It should be noted that, according to our estimations, the energy of fullerene formation from graphite is about 56 kJ/mol of carbon [32]. The comparison of these values suggests definite expectations concerning the possibility to obtain metastable diamond-like carbon modifications.

The formation energy of either fullerene molecules or clathrate carbon frameworks decreases due to the insertion of atoms into polyhedral voids. At present a large number of endofullerenes has been synthesized [33]. One of the mechanisms providing their formation is the capture of atoms or ions during the synthesis and the formation of carbon sphere. It is possible that a similar mechanism will take place during the formation of intercalation compounds with a carbon framework. The choice of possible "guests" to a great extent depends on geometric factors. The diameters of polyhedral voids in the CS-1 frameworks are 2.18 and 2.24 Å while in the CS-2 frameworks they are 2.18 and 2.62 Å which is much less than the diameter of the void in C_{60} molecule (5.68 Å). Because of this, the choice of "guests" for the preparation of compounds with these structures is much more limited than that for fullerenes. If we turn to the size of ions, we can state the possibility for the formation of intercalation compounds of such metals as lithium and beryllium in case if they are ionized in molecular voids. These compounds should be similar to the clathrates of carbon analogs with alkaline metals. They should also contain two weakly interacting subsystems of valence electrons as electron pairs localized along the edges of polyhedra and the delocalized electrons of the guest that provide metal conductivity of the clathrate. An increase in the size of void leads, on the one hand, to the increase in the energy of formation of the carbon framework, on the other hand, it broadens the choice of "guests". Because of this, it cannot be excluded that a more stressed framework would turn out to be more favourable for the formation of intercalation compounds than a framework which is less stressed but contains smaller voids. Because of this, it is reasonable to calculate the structure and to estimate the energy of the formation of lattices with large voids. We selected carbon framework with the HS structure as an example. This structure was observed for the first time in clathrasile and called "dodecasile 1H" [34]; later on, isostructural clathrate hydrates were discovered [16, 35].

The HS framework is composed of polyhedra $5^{12}6^8$, $4^35^66^3$ and 5^{12} at the ratio of 1 : 2 : 3; the number of water molecules in the unit cell is 34. This framework can be considered as the packing of polyhedral layers of two types (Fig. 3) [30]. The layer B is built of the polyhedra $5^{12}6^8$ and $4^35^66^3$ at a ratio of 1 : 2; their centres are situated in the nods of 3^6 net. The centres of polyhedra 5^{12} of the α layer are located in the nods of the 3636 kagome net. The spatial lattice is formed by packing the layers $B\alpha B\alpha\ldots$.

The procedure for the calculation of quantitative parameters of the structure of aqueous clathrate framework with the HS-3 and its energy are presented in [36]. We used this technique to calculate an isostructural carbon framework. Power constants are taken from [31]. The coordinates of the basic atoms designated in [36] are found to be: $x_1 = 0.2106$, $z_1 = 0.2241$, $x_2 = 0.3863$, $z_2 = 0.3612$, $x_3 = 0.1319$, $z_4 = 0.1364$. Lattice parameters are: $a = 6.817$ Å, $c = 5.548$ Å. Bond lengths are varied within the range of 1.513−1.557 Å and valence angles in pen-

tagonal faces are varied from 106.40 to 108.57º. The deformation energy for valence bonds and angles during the formation of diamond-type framework are 0.68 and 38.51 kJ/mol, respectively. The total energy of the phase transition und r consideration is 39.19 J/mol. So, this framework is much more stressed than CS-1 and CS-2; however, the energy of its formation from diamond is nevertheless lower than the energy of fullerene formation from graphite.

CONCLUSION

Recent discovery of fullerenes and nanotubulenes helped to state that sp^2 carbon atoms are able to form various structures. Similar properties were not observed for tetrahedrally coordinated carbon atoms. However, reliable grounds suggest that in future it would be possible to obtain various crystal structures built of the atoms with sp^3-coordination. Really, there are topological reasons for the existence of various polyhedral frameworks which are regular or irregular packings of polyhedra with cubic vertexes. The existence of clathrate compounds of the carbon analogs creates also chemical grounds allowing one to state that the synthesis of such structures is possible. So, it is possible that in future new polymorphous modifications will be discovered that would be built of sp^3-coordinated carbon atoms. They would form structural series of clathrate diamonds. Intercalation of small ions into their voids will allow to obtain new compounds (doped clathrate diamonds) with an unusual set of properties.

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