

INVITED LECTURES

POSSIBLE WAYS OF MINI-FULLERENE FORMATION: FROM FOUR TO TWENTY

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I. INTRODUCTION

It is customary to assume that fullerenes are the carbon molecules having a shape close to a spherical surface which can be composed of regular pentagons combined with regular hexagons. From this it follows that the least fullerene has twenty atoms forming twelve pentagons. We have supposed that this restriction is unnecessary [1]. In other words, we have taken the term “*fullerene*” in a broad sense as any convex shape inscribed into a spherical surface which can be composed of atoms, each atom having *three nearest neighbors*, as in usual fullerenes, whenever discussing hollow carbon clusters. This geometrical approach allowed us to obtain possible forms of the broad-sense fullerenes. To gain a more penetrating insight into their nature, we have also taken into consideration, along with the atomic structure of these spherical molecules, their electronic structure [2]. For this purpose we have developed an enlarged version of the theory by Sidgwick and Powell [3] according to which:

- Geometry of a molecule is dictated by the arrangement of electron pairs in the valence shell of atoms;
- Each shared electron pair, forming a covalent bond, can be considered as a point charge;
- All the electron pairs of a molecule arrange themselves into such configuration which ensures their equal and maximal removing from each other.

Sidgwick–Powell’s theory, created in 1940, allowed explaining and predicting stereochemical properties of many simple molecules (more than 1500 [3]). This theory was extended in the twenty-first century and applied to cyclic molecules such as cyclohexane [4] and usual fullerenes [5], which have no a central atom. The all-important result of such extension consists in the following: *the hidden symmetry of special electronic pattern does not coincide with that of atomic one*. However, it is precisely *the electronic pattern that defines the atomic structure*.

The modified approach developed in [4] was applied to the broad-sense fullerenes [1]. Contrary to the previous approaches [3, 4], where atoms and electron pairs had their own spheres, the main innovation in [1] is the additional postulate:

- Atoms and shared electron pairs, forming covalent bonds, are located *on one and the same sphere*.

It follows herefrom that the geometry of both the electronic structure as well as of the atomic structure of fullerenes can be most conveniently constructed and studied with the help of *spherical geometry*.

Up to now mechanism of fullerene formation is unclear. The irrefutable fact is as follows. If to take one electrode of ${}^6\text{C}^{13}$ graphite and another of ordinary ${}^6\text{C}^{12}$ graphite, the fullerene, formed in an electric arc, has ${}^6\text{C}^{13}$ – and ${}^6\text{C}^{12}$ – atoms arranged on a fullerene surface in random way. It follows herefrom that fullerene assemblage originates from separate atoms (or maybe from C_2 fragments).

In this contribution we used this fact and the approach developed in [1] as the basis for predicting possible ways of broad-sense fullerenes formation. Besides, as in [6], we have used graph theory [7] to represent formation of carbon clusters, their transformation from a cluster to a fullerene, and their final configurations.

II. TETRAHEDRAL FULLERENE C_4

Let us start with a reaction-active single carbon atom. One can envision two ways of forming a cluster of four carbon atoms (Figs. 1a, 1b). Consider the first way which incorporates three stages (Fig.

1a). In the first stage the single atom adds another atom and activates it. In its turn the second atom adds two other atoms, forming a simple branching. The second way consists of two stages (Fig. 1b). Here the reaction-active atom adds at once three atoms which create covalent connected pairs. If the process starts with a reaction-active carbon dimer (Fig. 1c), we have only two stages. At the first one each dimer atom adds other atoms; then mutual turning of the covalent bonds formed leads to arranging a tetrahedron. In all the cases the process consists of several stages which can differ, but the final configuration due to folding is one and the same tetrahedron. It can be represented with one of isomorphic graphs having four vertices (Figs. 1d, 1e).

It should be noted that the diagram shown in Fig. 1a is identical with one of the diagram (simple branching) illustrating formation process not only of an athermal tetravacancy under irradiation but also that of a branched polymer during polymerization [6].

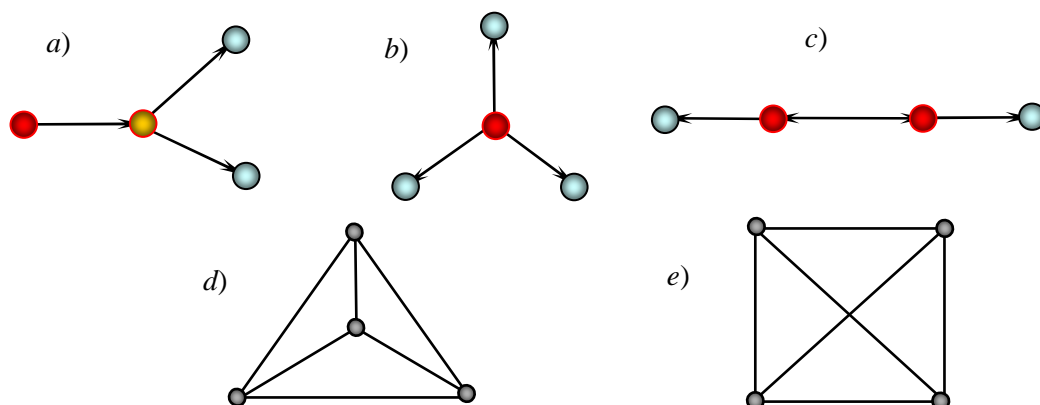


Figure 1 – Different ways of forming a cluster of four carbon atoms (*a, b, c*) and graph representation of a tetrahedral fullerene in the form of isomorphic graphs (*d, e*).

Consider the transform of a carbon cluster into a tetrahedron. According to our postulate, each carbon atom can have, as usual fullerenes, three neighbors who are located with the nucleus atom on one and the same sphere (Fig. 2a). Here the large circles represent carbon atoms; the small ones refer to electron pairs. In other words, we have a cluster with three covalent bonds; the tail atoms having unshared electron pairs which also lie on a sphere. If the growth of this cluster is suppressed, the tail atoms, due to the interaction of their unshared electron pairs (Fig. 2b), create covalent bonds between themselves fashioning a tetrahedron (Fig. 2c). It should be emphasized that in the qualitative theory by Sidgwick and Powell it is supposed that any electron pairs, shared or unshared, can only repel, but not attract. This restriction is a consequence of the assumption that the electron pairs can be considered as point charges. More careful quantitative analysis on the basis of dynamics reveals that it is necessary to take into account eigenvibrations of an electron pair considering the electron pair as a dynamic variable [2].

With this in mind, we have shown that each pair plays the role of an external field with respect to another pair, thus polarizing it. Therefore the electron pair is a dynamic electric dipole rather than a quasi-point electric charge. Such dipole represents itself to be an oscillator, i.e. the system of two opposite point charges which are equal in absolute value; the distance between them is changing in consequence of vibrations near a stable equilibrium position. As a result, there appeared intramolecular van der Waals interaction between the electron pairs. It follows herefrom an essential difference between static charges and dynamic dipoles. The first produce only Coulomb repulsion whereas the second both repulsion and van der Waals attraction. It is just this attraction which leads to producing the tetrahedral fullerene (Fig. 3a), having the electronic structure in the form of an octahedron (Fig. 3b). According to [8] an octahedron is the only stable configuration for six electron pairs.

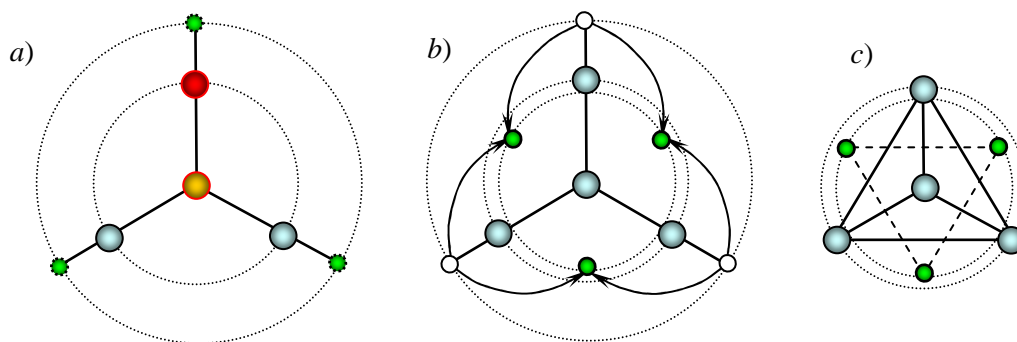


Figure 2 – Top view: (a) cluster of four carbon atoms, each tail atom having an unshared electron pair; formation of new covalent bonds (b) gives rise to a tetrahedron (c). Atomic and electronic parallels are shown by dotted circles. The edge length of the tetrahedron is a ; the radius of the atomic parallel is $a / \sqrt{3}$; the radius of the electronic parallel is $a / 2$.

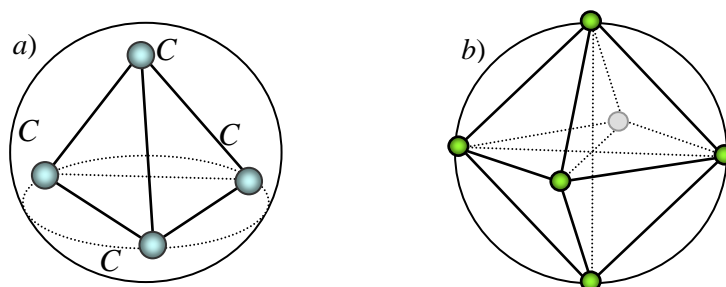


Figure 3 – Carbon tetrahedron inscribed into a sphere (a); here any three atoms lie on one and the same parallel; (b) shared-electron-pairs octahedron corresponding to (a).

III. TRIANGULAR PRISMATIC FULLERENE C_6

The next in size carbon cluster, each atom of it having three nearest neighbors, which can be inscribed into a sphere, is a triangular prism. Similar to the previous procedure for a tetrahedral fullerene, we can envision different ways of forming at first a cluster of six carbon atoms (Figs. 4a through d) and then a triangular-prism fullerene as two graphs having six vertices (Figs. 4e, 4f). It should be noted that these graphs are isomorphic [7].

It should be noted that from a mathematical viewpoint the diagram (a) is identical with one of the diagram (double branching) illustrating formation process not only of an athermal hexavacancy at irradiation but also of a branched polymer at polymerization [6].

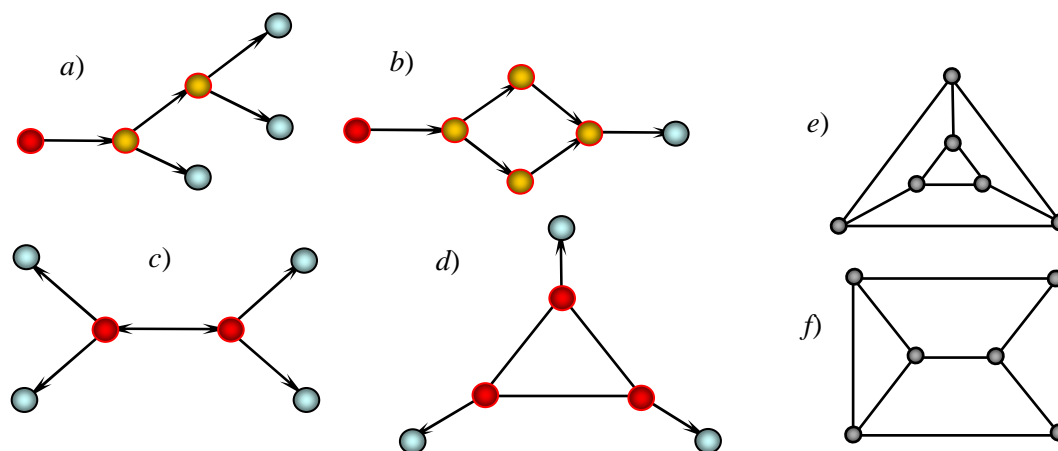


Figure 4 – Different ways of forming a cluster of six carbon atoms (a, b, c, d) and graph representation of a triangular-prism fullerene in the form of isomorphic graphs (e, f)

Due to the attraction of electron pairs, there forms the triangular-prism (Fig. 5a), having the electronic structure in the form, which contains nine point charges with maximum removal from each

other (Fig. 5b). The electronic configuration of this mini-fullerene coincides with that of an ordinary molecule having nine electron pairs in its valence shell [8]. For this reason we will use the terminology accepted in molecular geometry. According to [8] this configuration is named a three-cap trigonal prism.

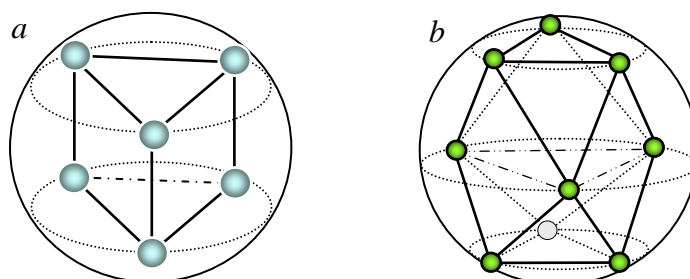


Figure 5 – Carbon triangular prism inscribed into a sphere. Here (a) three atoms of two bases lie on one and the same parallel; (b) nine shared electron pairs on a sphere surface with maximum removal from each other, so called a three-cap trigonal prism.

Because of the page restriction we limited ourselves by these two examples of mini-fullerene formation; other examples will be given during the workshop.

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