

Chapter 2

Origami: Self Organizing Polyhexagonal Carbon Structures for Formation of Fullerenes, Nanotubes and Other Carbon Structures

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Abstract The selective production of fullerenes and nanotubes is a challenging problem. Molecular dynamics calculations can reveal the physical and chemical properties of various carbon nanostructures and can help to devise the possible formation pathways. In our previous publications we have presented various graphene patterns which could transform in a self organising way into the desired structure. The processes were realized in molecular dynamics simulations. In the present publication we review the molecular dynamics method used in our previous calculations and give further graphene patterns for C_n fullerenes from C_{60} to C_{100} . Also the possibility of experimental realizations will be discussed.

2.1 Introduction

The idea of graphene origami emerged already nearly a decade before the famous graphene paper was published in 2004 (Novoselov et al. 2004). In 1995 Ebbesen and Hiura published namely an article with the title: “Graphene in 3-Dimension: toward graphite origami” (Ebbesen and Hiura 1995). These authors suggested that graphene could be folded up to a variety of shapes and cutting well-defined patterns can allow to design nanotubes with given diameters. Even earlier Kroto et al. wrote in their “ C_{60} :Buckminsterfullerene” paper (Kroto et al. 1985): “Our rationalization of these results is that in the laser vaporization, fragments are torn from the surface as pieces of the planar graphite fused six-membered ring structure. We believe that the distribution is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters

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equilibrate by two- and three-body collisions towards the most stable species, which appears to be unique cluster containing 60 atoms.”

These early suggestions, however, were based on larger graphene sheets in the case of nanotubes or they supposed degradation or fusion of various ring fragments. In our recent molecular dynamics simulations we have shown the existence of various patterns cut out from the graphene which transformed to C_{60} and C_{70} fullerenes or nanotubes depending on the initial pattern structures (László and Zsoldos 2012a, b, 2014). The greater application of fullerenes and nanotubes faces the lack of selective growth and assembly processes. Our results can initiate new experimental researches for improving the existing carbon nanostructure productions and to develop a new, structure selective nanolithography of fullerenes, nanotubes and other carbon structures. We are aware of the fact that nowadays patterning of graphene is not yet at atomic precision, but there are promising experimental achievements (Avouris et al. 2007; Chen et al. 2007; Tapasztó et al. 2008; Feng et al. 2012).

First we review the molecular dynamics method which was used in our previous calculations (László and Zsoldos 2012a, b, 2014), after the methods of experimental patterning will be shown. Then we present various geometrical patterning of graphene which are not applicable for self organizing production of fullerenes. Than we present the method of coding the final structure in the initial one. As new results we suggest new patterns for formation of C_n fullerenes with ($72 \leq n \leq 100$). In the conclusion we analyse our results and regarding new experimental results we extend the meaning of patterning to hydrocarbon patterns as well.

2.2 Tight Binding Molecular Dynamics Calculation

Although our system contained only about 100 carbon atoms we were using a tight binding method in our molecular dynamics simulations as we had to make a great number of runs. The inter atomic forces were calculated with the help of a density functional tight binding (DFTB) model (Porezag et al. 1995). In such a model the total energy is written in the form of

$$E = \sum_{k=1}^N \frac{p_k^2}{2M_k} + E_{\text{bond}} + E_{\text{rep}} \quad (2.1)$$

where

$$E_{\text{bond}} = \sum_i n_i \varepsilon_i \quad (2.2)$$

is the tight binding electronic energy where the summation goes over all of the eigenstates of the tight binding Hamiltonian matrix H . The value n_i of the occupation number is 2, 1 or 0 depending of the occupation of the eigenfunctions

$$\psi_i(\mathbf{r}) = \sum_v^m C_{vi} \phi_v(\mathbf{r} - \mathbf{R}_v) \quad (2.3)$$

Here the atom-centred basis function $\phi_v((\mathbf{r}-\mathbf{R}_v))$ is centred around the atom with the position vector $\mathbf{R}_v$ and m equals to the number of basis functions centred on the atoms in the positions $\mathbf{R}_k$ with $1 \leq k \leq N$ where N is the number of atoms and $\mathbf{R}_v$ equals to one of the vectors $\mathbf{R}_k$. $\mathbf{P}_k$ is the momentum of the atom k with the mass M_k . The eigenvalues and the eigenvectors are determined by the equations

$$\sum_{v=1}^m C_{vi}(H_{\mu v} - \varepsilon_i S_{\mu v}) = 0 \quad (2.4)$$

For each μ and i , where

$$H_{\mu v} = \langle \phi_\mu | H | \phi_v \rangle \quad (2.5)$$

and

$$S_{\mu v} = \langle \phi_\mu | \phi_v \rangle \quad (2.6)$$

is the overlap integral. The $H_{\mu v}$ and $S_{\mu v}$ off diagonal matrix elements are given with the help of the function $H_{sp\sigma}(R)$, $H_{pp\sigma}(R)$, $H_{ss\sigma}(R)$, $H_{pp\pi}(R)$, $S_{sp\sigma}(R)$, $S_{pp\sigma}(R)$, $S_{ss\sigma}(R)$, $S_{pp\pi}(R)$. Namely we were using only carbon atoms and each of them was supplied by one sorbital and three p orbital. That is ϕ was s, p_x , p_y or p_z orbital. The corresponding functions are given in ref. (Porezag et al. 1995) with the help of Chebyshev polynomials. The matrix element were given with the help of the Slater-Koster relations (Slater and Koster 1954).

$$H_{ss}(\mathbf{R}_j - \mathbf{R}_i) = H_{ss\sigma}(R_{ij}) \quad (2.7)$$

$$H_{sx}(\mathbf{R}_j - \mathbf{R}_i) = \cos(\alpha_x)H_{sp\sigma}(R_{ij}) \quad (2.8)$$

$$H_{xx}(\mathbf{R}_j - \mathbf{R}_i) = \cos^2(\alpha_x)H_{pp\sigma}(R_{ij}) + (1 - \cos^2(\alpha_x))H_{pp\pi}(R_{ij}) \quad (2.9)$$

$$H_{xy}(\mathbf{R}_j - \mathbf{R}_i) = \cos(\alpha_x)\cos(\alpha_y)H_{pp\sigma}(R_{ij}) - \cos(\alpha_x)\cos(\alpha_y)H_{pp\pi}(R_{ij}) \quad (2.10)$$

$$H_{xz}(\mathbf{R}_j - \mathbf{R}_i) = \cos(\alpha_x)\cos(\alpha_z)H_{pp\sigma}(R_{ij}) - \cos(\alpha_x)\cos(\alpha_z)H_{pp\pi}(R_{ij}) \quad (2.11)$$

Here we have supposed that the atomic orbital ϕ_μ was centred at $\mathbf{R}_i$ and the atomic orbital ϕ_v was centered on the atom at $\mathbf{R}_j$. The direction cosines of the vector $\mathbf{R}_j - \mathbf{R}_i \neq 0$ are $\cos(\alpha_x)$, $\cos(\alpha_y)$ and $\cos(\alpha_z)$. R_{ij} is the distance between the two atoms. If the atomic orbitals ϕ_μ and ϕ_v are centred on the same atom, $H_{ss} = -13.573eV$ and $H_{xx} = H_{yy} = H_{zz} = -5.3715eV$ for $\mu = v$ and $H_{\mu v} = 0$ for $\mu \neq v$. The other matrix elements can be generated with the help of symmetry.

Similar relations are valid for the $S_{\mu v}$ overlap matrix elements as well. That is,

$$S_{ss}(\mathbf{R}_j - \mathbf{R}_i) = S_{ss\sigma}(R_{ij}) \quad (2.12)$$

$$S_{sx}(\mathbf{R}_j - \mathbf{R}_i) = \cos(\alpha_x)S_{sp\sigma}(R_{ij}) \quad (2.13)$$

$$S_{xx}(\mathbf{R}_j - \mathbf{R}_i) = \cos^2(\alpha_x)S_{pp\sigma}(R_{ij}) + (1 - \cos^2(\alpha_x))S_{pp\pi}(R_{ij}) \quad (2.14)$$

$$S_{xy}(\mathbf{R}_j - \mathbf{R}_i) = \cos(\alpha_x) \cos(\alpha_y) S_{pp\sigma}(\mathbf{R}_{ij}) - \cos(\alpha_x) \cos(\alpha_y) S_{pp\pi}(\mathbf{R}_{ij}) \quad (2.15)$$

$$S_{xz}(\mathbf{R}_j - \mathbf{R}_i) = \cos(\alpha_x) \cos(\alpha_z) S_{pp\sigma}(\mathbf{R}_{ij}) - \cos(\alpha_x) \cos(\alpha_z) S_{pp\pi}(\mathbf{R}_{ij}) \quad (2.16)$$

for basis functions centred on different atoms and if the two basis functions are centred on the same atom, $S_{ss} = S_{xx} = S_{yy} = S_{zz} = 1$ if $\mu = \nu$ and $S_{\mu\nu} = 0$ for $\mu \neq \nu$.

The E_{rep} repulsive par potential is also given in ref. (Porezag et al. 1995) with the help of Chebyshev polynomials.

The atomic force

$$\mathbf{F}_k = - \sum_i \sum_{\mu,\nu}^m n_i \left(C_{i\mu} C_{i\nu} \left[\frac{\partial H_{\mu\nu}}{\partial \mathbf{R}_k} - \varepsilon_i \frac{\partial S_{\mu\nu}}{\partial \mathbf{R}_k} \right] \right) - \frac{\partial E_{\text{rep}}}{\partial \mathbf{R}_k} \quad (2.17)$$

is calculated from the Hellmann-Feynman theorem.

In the canonical ensemble molecular dynamics calculations the constant environmental temperature was controlled with the help of Nosé-Hoover thermostat (Nosé 1984; Hoover 1985; Allen and Tildesley 1996; Frenkel and Smit 1996). In this thermostat the environmental temperature is T_{env} , and the force acting on the atom in the position $\mathbf{R}_k$ is determined as

$$\mathbf{F}_k^{\text{NH}} = - \sum_i \sum_{\mu,\nu}^m n_i \left(C_{i\mu} C_{i\nu} \left[\frac{\partial H_{\mu\nu}}{\partial \mathbf{R}_k} - \varepsilon_i \frac{\partial S_{\mu\nu}}{\partial \mathbf{R}_k} \right] \right) - \frac{\partial E_{\text{rep}}}{\partial \mathbf{R}_k} - \xi \mathbf{P}_k \quad (2.18)$$

The friction coefficient ξ is given by the first-order differential equation

$$\dot{\xi} = \frac{f}{Q} k_B (T - T_{\text{env}}) \quad (2.19)$$

where k_B is the Boltzmann constant, Q is a thermal inertial parameter, $f = 3N$ is the number of degrees of freedom and the kinetic temperature is

$$T = \frac{1}{3Nk_B} \sum_{k=1}^N \frac{\mathbf{P}_k^2}{2M_k} \quad (2.20)$$

The thermal inertial parameter determines the time scale of the kinetic temperature oscillation and strength of interaction with the environment. The detailed nature of the dynamics depends on the value of Q chosen but the average properties are less sensitive to its value, thus it can be arbitrary.

The equation of motion was solved with the help of the Verlet algorithm (Verlet 1967)

$$\mathbf{V}_k(t) = \frac{\mathbf{R}_k(t + \Delta t) - \mathbf{R}_k(t - \Delta t)}{2\Delta t} \quad (2.21)$$

$$\mathbf{P}_k(t) = M_k \mathbf{V}_k(t) \quad (2.22)$$

$$R_k(t + \Delta t) = 2R_k(t) - R_k(t - \Delta t) + \frac{F_k^{NH}(t)}{M_k} \Delta t^2 \quad (2.23)$$

where Δt is the time step. The Euler algorithm

$$\xi(t) = \xi(t - \Delta t) + \frac{f}{Q} k_B (T(t) - T_{env}) \Delta t \quad (2.24)$$

gives the solution of the friction coefficient ξ .

2.3 Patterning of Graphene

2.3.1 Experimental Patterning

Patterning of graphene comes from the need of constructing graphene based electronic devices. Although the flat and wide graphene is semimetal, the band gap of nanoribbons scales inversely with their widths (Feng et al. 2012). The graphene patterning methods are the electron and/or ion beam irradiation (Chen et al. 2007; Fischbein and Drndić 2008; Meyer et al. 2008; Huang et al. 2009; Girit et al. 2009; Lemme et al. 2009; Bell et al. 2009; Huang et al. 2010; Shi et al. 2011; Song et al. 2011) the scanning tunnelling lithography (McCarley et al. 1992; Hiura 2004; Tapasztó et al. 2008) and various etching techniques (Zhang et al. 2011; Han et al. 2007; Bai et al. 2009, 2010; Kim et al. 2012; Sinitskii and Tour 2010; Li 2008; Datta et al. 2008; Ci et al. 2008; Dimiev et al. 2011; Kosynkin 2009; Jiao et al. 2009, 2010). In electron beam lithography nanoribbons with a width of 10–15 nm were fabricated (Chen et al. 2007; Han et al. 2007). Scanning tunnelling microscope lithography reached the nanoribbon width of 2.5 nm (Tapasztó et al. 2008).

With redesigned zinc patterns single atomic layer resolution lithography was found on graphene (Björk et al. 2011).

2.3.2 Geometrical Patterning Including Multiples of Some Atoms

Many authors working on carbon nanostructures start their talks with a picture presenting a graphene sheet containing various cut out patterns which are turning into fullerenes and nanotubes (Geim and Novoselov 2007). These processes follow the text book geometric construction of fullerenes and nanotubes and explain the fact that the graphene is “Mother of all graphitic forms” (Geim and Novoselov 2007). Following the mathematical construction these initial patterns contain usually more carbon atoms than needed in the final structure. Several of these atoms are identified during the geometric constructions. Beaton for example presented patterns which could be transformed into fullerenes by further cutting along given lines and

cut out of hexagons. The fullerenes were obtained by overlapping and gluing given hexagons (Beaton 1995). In the projection method the pentagons of the fullerenes are constructed from the honeycomb lattice by removing a triangular region (Dresselhaus et al. 1996). The nanotubes can be imagined as rolled up parallelograms or nanoribbons (Dresselhaus et al. 1996). In all of the previous graphene patterns the initial structures have more carbon atoms than the final fullerene or nanotube. Thus they can not be used as self organizing patterns.

2.3.3 Geometrical Patterning for Self Organizing Processes

We are looking for patterns which have the same number of carbon atoms as the final structure and they can be transformed into the desired arrangement in a self organizing way.

In biology the information is encoded in the amino acid sequence. This sequence determines the structure and properties of the protein. In our previous publications (László and Zsoldos 2012a, b, 2014) the final structure of the fullerenes and nanotubes was coded in the geometrical structure of the graphene patterns. The conditions of the coding were the followings: (1) A pattern contains only hexagons. (2) There are some fourth neighbouring atoms on the perimeter which can approach each other during their heat motion by constructing new pentagonal or hexagonal faces. (3) After the formation of new faces other carbon atoms will be in appropriate positions to produce new bonds. Repeating steps (2) and (3) we obtain the final structure selected by the initial pattern.

In Figs. 2.1–2.17 we present 17 examples of isolated pentagon C_n fullerenes for each possible even values of n in the ranges ($n = 60$) and ($70 \leq n \leq 100$). These patterns fulfil the above mentioned conditions. Applying the isolated-pentagon rule (IPR) there is only one isomer for C_{60} , C_{70} , C_{72} and C_{74} . For ($62 \leq n \leq 68$) there is not any fullerene having the IPR. As n increases, the number of isomers increases significantly. For ($n = 76$) the number of isomers is two only, but for ($n = 100$) it reaches the value of 450 (Fowler and Manolopoulos 1995). In Figs. 2.1–2.17 also the Schlegel diagrams of the corresponding fullerenes are presented with the cut out pattern in the Schlegel diagram and the same cut out pattern in the graphene sheet. For the notation of the fullerenes and the spiral codes we used the definitions given in reference (Fowler and Manolopoulos 1995).

In tight binding molecular dynamics simulations the patterns of Figs. 2.1 and 2.2 developed into the desired C_{60} and C_{70} fullerenes (László and Zsoldos 2012a, b, 2014). In these publications the possibility of transforming into the desired structures was presented several fullerene and nanotube patterns. These processes were controlled by applying appropriate environmental temperature conditions in the frame work of the Nosé-Hoover thermostat.

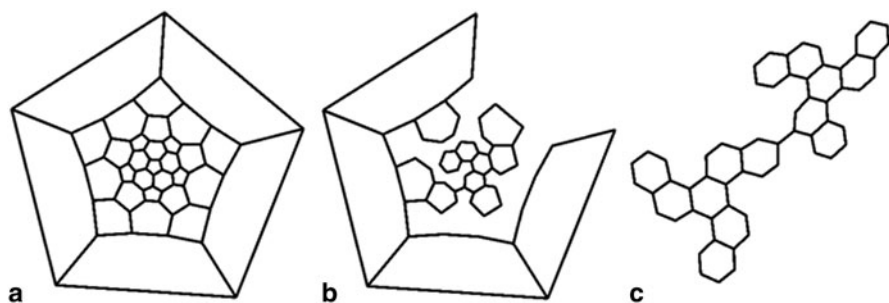


Fig. 2.1 The C_{60} fullerene of symmetry I_h and ring spiral (1,7, 9,11, 13,15, 18,20, 22,24, 26,32). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

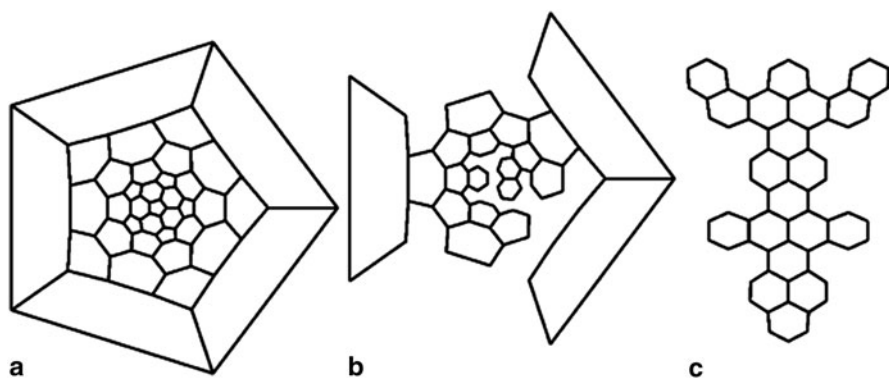


Fig. 2.2 The C_{70} fullerene of symmetry D_{5h} and ring spiral (1,7, 9,11, 13,15, 27,29, 31,33, 35,37). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

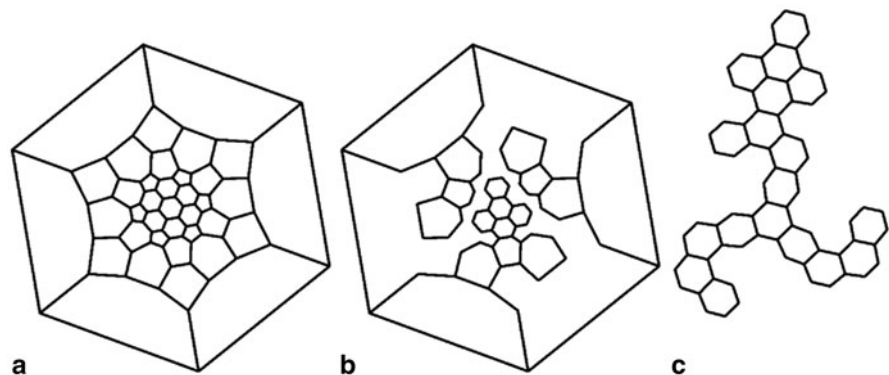


Fig. 2.3 The C_{72} fullerene of symmetry D_{6d} and ring spiral (1,7, 9,11, 13,18, 22,24, 27,34, 36,38). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

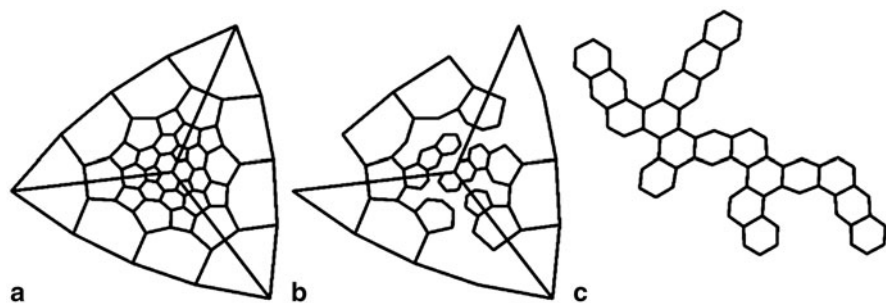


Fig. 2.4 The C_{74-1} fullerene of symmetry D_{3h} and ring spiral (1,7, 9,11, 14,23, 26,28, 30,32, 35,38). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

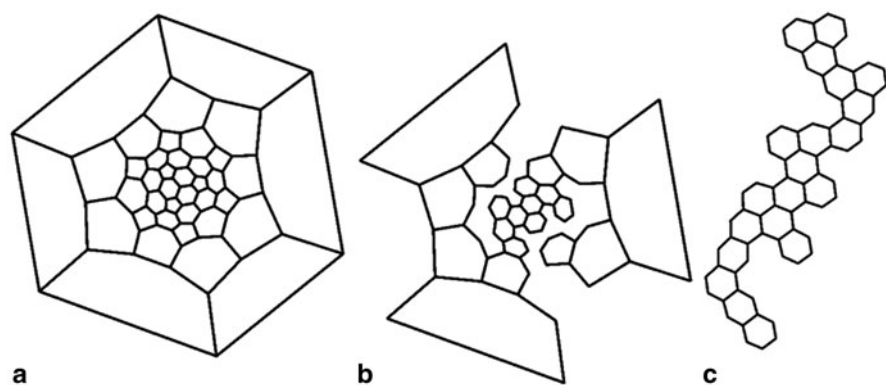


Fig. 2.5 The C_{76-2} fullerene of symmetry T_d and ring spiral (1,7, 9,12, 14,21, 26,28, 30,33, 35,38). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

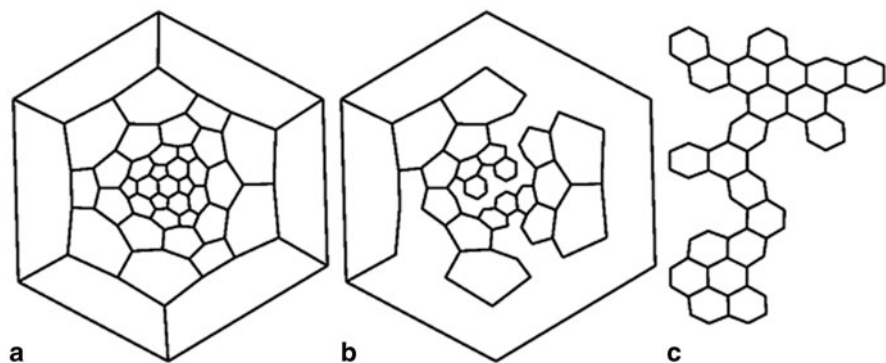


Fig. 2.6 The C_{78-4} fullerene of symmetry D_{3h} and ring spiral (1,7, 9,11, 15,18, 22,25, 33,37, 39,41). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

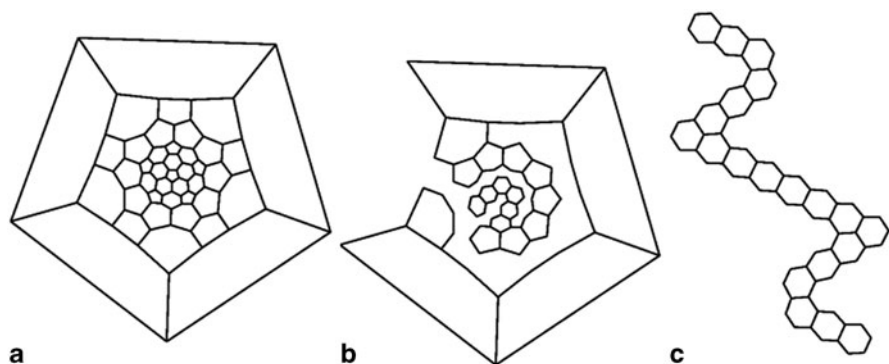


Fig. 2.7 The $C_{80,6}$ fullerene of symmetry D_{5h} and ring spiral (1,7, 10,12, 14,19, 26,28, 32, 34, 39,42). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

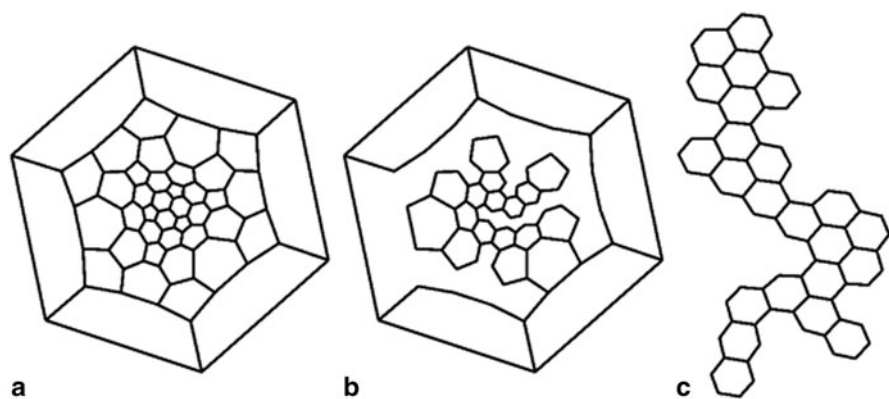


Fig. 2.8 The $C_{82,7}$ fullerene of symmetry C_{3v} and ring spiral (1,7, 9,12, 14,20, 27,32, 34,36, 38,40). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

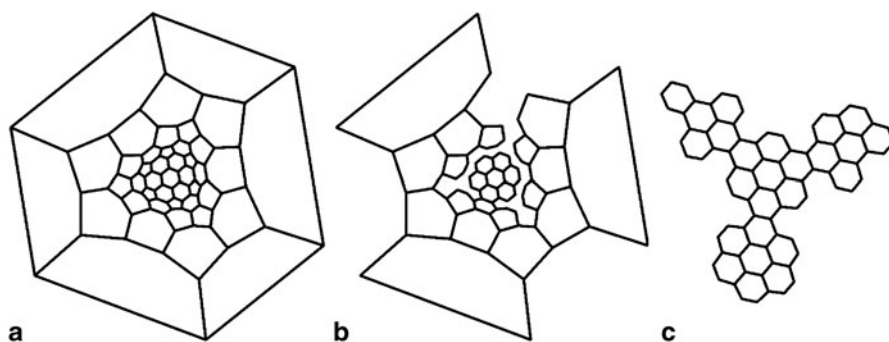


Fig. 2.9 The $C_{84,20}$ fullerene of symmetry T_d and ring spiral (1,7, 9,13, 20,23, 25,28, 33,37, 39,41). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

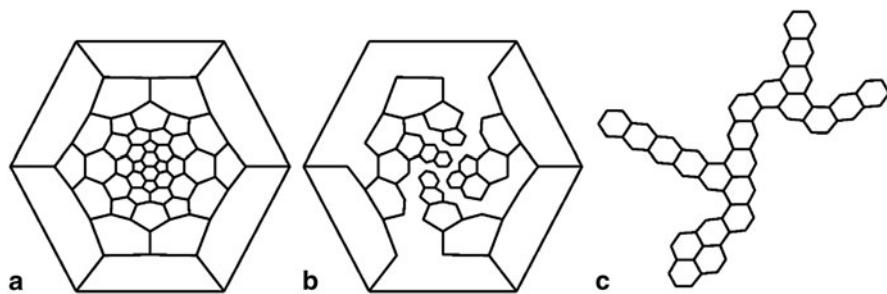


Fig. 2.10 The C_{86_9} fullerene of symmetry C_{2v} and ring spiral (1,7, 9,11, 23,25, 27,29, 33,41, 43,45). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

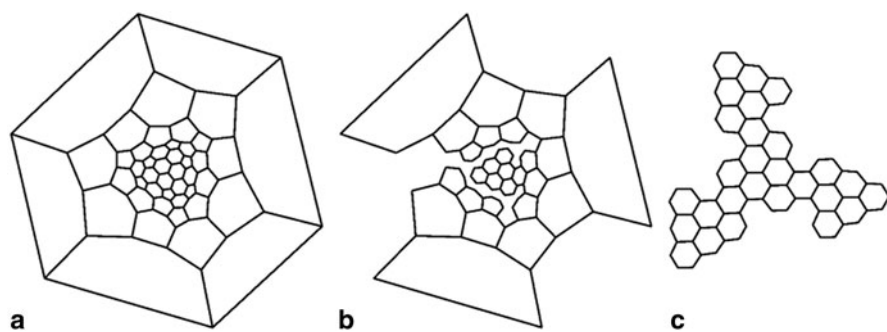


Fig. 2.11 The $C_{88_{34}}$ fullerene of symmetry T and ring spiral (1,7, 9,12, 24,27, 31,33, 35,38, 40,42). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

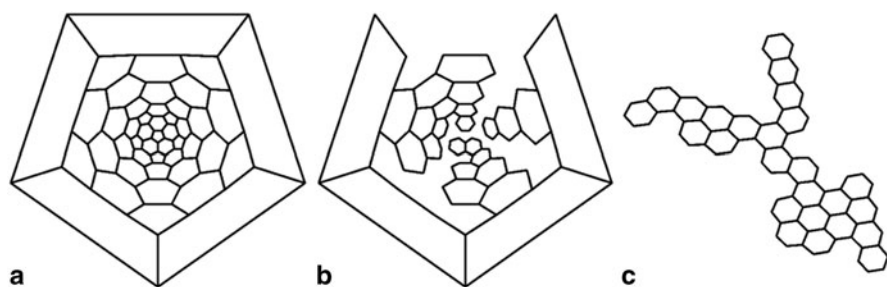


Fig. 2.12 The C_{90_1} fullerene of symmetry D_{5h} and ring spiral (1,7, 9,11, 13,15, 37,39, 41, 43, 45,47). The Schlegel diagram (a), the pattern in the Schlegel diagram (b), the pattern in the graphene lattice

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