Flattened fullerenes*

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Quantum-chemical calculations of giant flattened fullerenes C_n (lentil-shaped) have been carried out. The topology, molecular and electronic structure of these fullerenes have been studied. Such molecules consist of two identical coronenoid fragments of a graphite layer, which are arranged one above the other, and a system of polycondensed five- and six-membered cycles, which form a side surface of the cluster. Polyhedral structures with isolated pentagons of three symmetry types (D_{6h}, D_{6d}, and D_{3h}) have been considered. The topology of these structures is described in terms of planar molecular graphs. Electronic structures of eleven flattened lentil-shaped C_n clusters (n = 72—216) have been studied in the π approximation. Most of the considered systems have closed or quasi-closed electron shells (according to Hückel) and rather large energy gaps separating the highest occupied and lowest unoccupied MO, which is indicative of their kinetic stability. Fragments of the potential energy surfaces of the C_{72} and C_{96} fullerenes have been studied by the MNDO, AM1, and MNDO/PM3 methods. For the C_{96} cluster, two local energy minima, which correspond to the lentil-shaped isomers with D_{6h} and D_{6d} symmetry, have been determined. As a result of optimization of geometric parameters, it was found that all three methods give close values of heights (H = 6.7 Å) and diameters (D = 9.8 Å) for both isomers. The clusters change to quasi-two-dimensional systems ($H \ll D$) with increasing sizes of coronenoid fragments.

Key words: fullerenes, polyhedral carbon clusters; quantum-chemical calculations, MNDO, AM1, and MNDO/PM3 methods.

The electric arc method is the most generally used and efficient method for synthesis of polyhedral carbon clusters with different molecular weights. In this case, molecules that are nearly spherical (C_{60}) or elongated in one direction (C_{70}) are most likely to be formed.[1–4] In the literature, single-layer and multilayer carbon structures of tubular (tubulenes) and onion-shaped types are also reported[5,6]; different hypotheses have been proposed about the possibility of the occurence of a variety of extended covalent structures consisting of fragments of fullerenes or tubulenes.[7–15]

When molecular forms of carbon are modeled, it is common practice to assume that the stability of polyhedral clusters with isolated five-membered cycles is determined to a large degree by their symmetry. Therefore, in most works on fullerenes, the main attention has been given to studies and prediction of properties of the clusters with icosahedral or tetrahedral symmetry or to elongated clusters with D_{5h} or D_{5d} symmetry.

The analysis of a multiple experimental data demonstrates that the type and structure of carbon materials are determined to a large degree by the conditions of their preparation. For example, it is known that some graphite samples are transformed to onion-shaped structures under the action of electron beam.[6] Therefore, it is not improbable that under certain conditions, synthesis of polyhedral carbon clusters, which are formed as a result of cross-linking of rather extended fragments of a graphite layer by border, is possible. These clusters may have a flattened shape and when the number of atoms is rather large, these clusters are transformed to quasi-two-dimensional graphite.

The main aim of this work is to discuss the method of generation of some symmetrical structures of this type and to evaluate the possibility of their occurrence.

Molecular design of lentil-shaped fullerenes

When modeling topological structures of flattened fullerenes, we shall describe them using planar molecular graphs, *i.e.*, Schlegel diagrams. Below, only such systems are considered, which are characterized by one of the following types of symmetry: D_{6h}, D_{6d}, or D_{3h}. We used molecular graphs of the coronenoid type as the basic structural units (according to the accepted nomenclature,[16] these systems belong to the class of graphs called rotographs).

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* Dedicated to Academician of the RAS N. S. Zefirov (on his 60th birthday).

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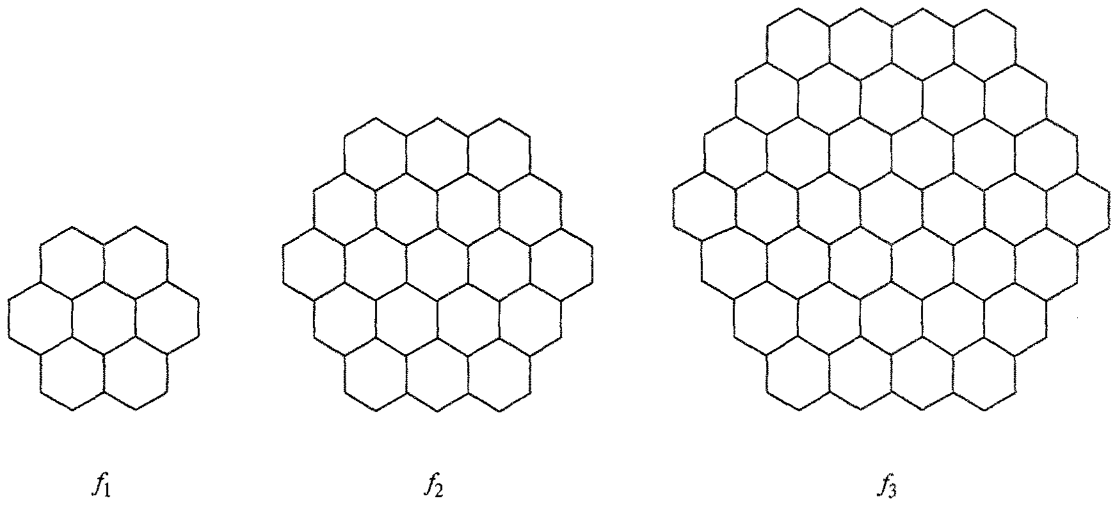

Fig. 1. Examples of coronenoid fragments.

Some of rotographs of the coronenoid type are shown in Fig. 1. To the initial term of the f_1 series there corresponds the molecular graph, which describes the carbon framework of the coronene molecule. The graph f_2 is obtained from f_1 as a result of bordering it by a cyclic layer, which consists of 12 hexagons. Similarly, each graph f_m is formed from the preceding f_{m-1} also using the procedure of bordering (the index m characterizes the number of cyclic layers, which encircle the central hexagon: the first, second, and third layers consist of 6, 12, and 18 rings, respectively; the m-th layer contains $6m$ hexagons). Molecular graphs f_1, f_2, and f_3, which are shown in Fig. 1, contain 24, 54, and 96 vertices, respectively.

Polyhedral clusters, which we shall consider below, are flattened (lentil-shaped). These polyhedra consist of two identical coronene fragments f_m, which are arranged one above the other, and the system of polycondensed

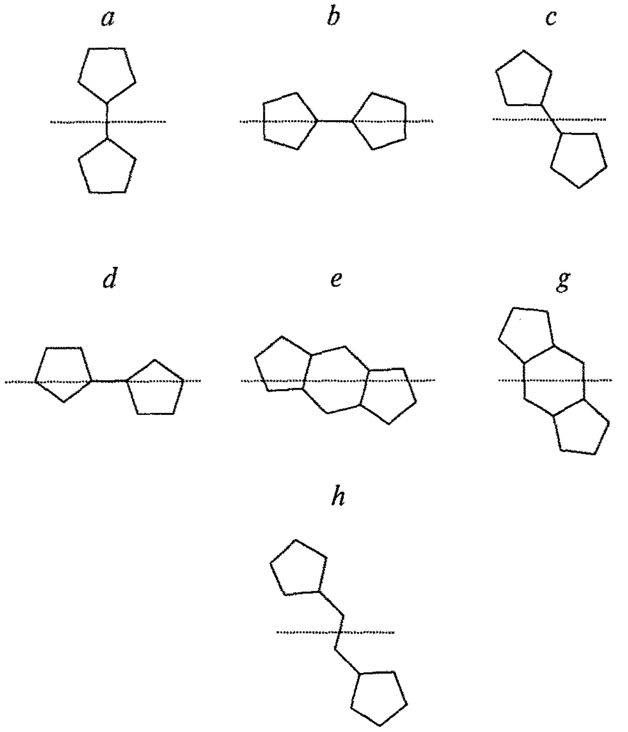

Fig. 2. Types of arrangement in pairs of five-membered cycles with respect to the equator in flattened fullerenes with D_{6h} and D_{6d} symmetry.

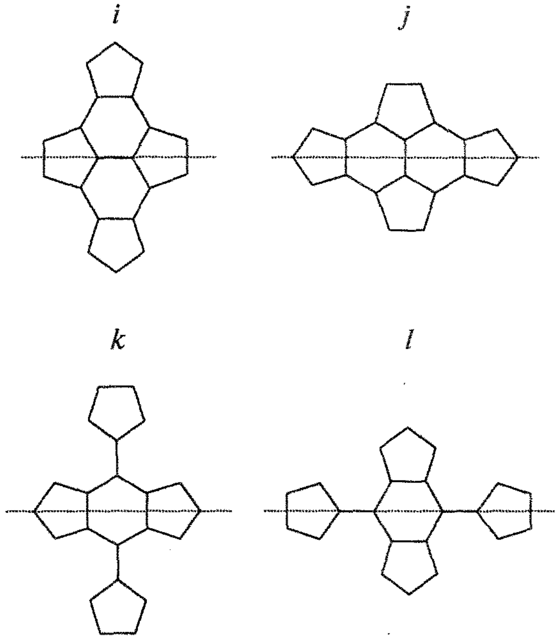

Fig. 3. Types of arrangement of five-membered cycles with respect to the equator in flattened fullerenes with D_{3h} symmetry.

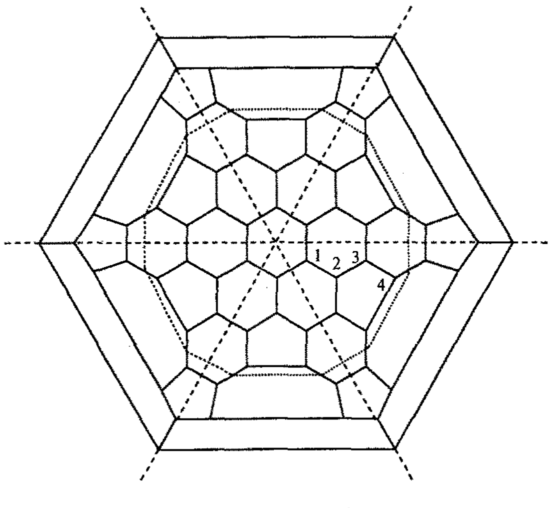

Fig. 4. Molecular graph for cluster **1**.

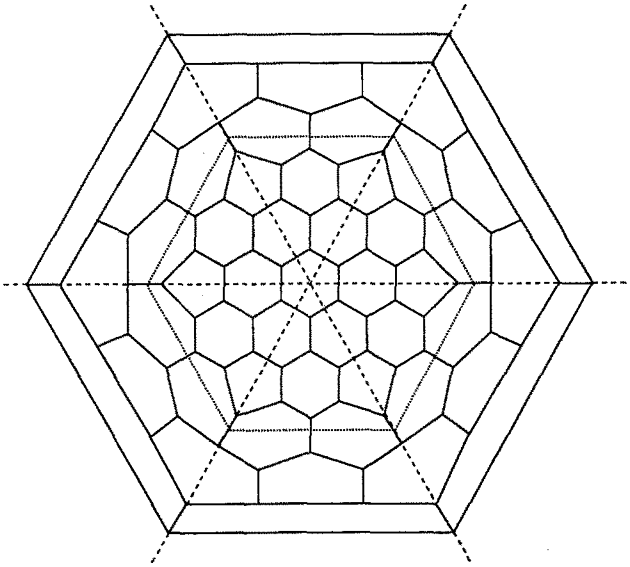

Fig. 5. Molecular graph for cluster **2**.

five- and six-membered carbon cycles, which form a side surface. All 12 pentagons of these polyhedra are located near the equatorial plane resulting in the flattened shape of these polyhedra. Note that the strains of torsion angles are minimum in coronenoid fragments. This should favor stabilization of polyhedral molecules under consideration.

Figure 2 presents several types of arrangement in pairs of pentagons in flattened polyhedral systems (D_{6h} or D_{6d} symmetry) with respect to the equator, which is indicated by a dotted line. When designing polyhedra with D_{3h} symmetry, we used three groups of fragments containing four pentagons each (Fig. 3). Molecular graphs for 11 lentil-shaped polyhedral clusters are shown in Figs. 4—14. It is evident from these figures that for any m, two graphite fragments f_m, arranged one above the other, can be completed to polyhedral clusters with D_{6h}, D_{6d}, or D_{3h} symmetry. Hereinafter, we shall use the following notation of clusters: C_n-(type of symmetry)-f_m-w, where n is the number of C atoms, f_m is a coronenoid fragment (see Fig. 1), and w is the type of arrangement of five-membered cycles (see Figs. 2 and 3).

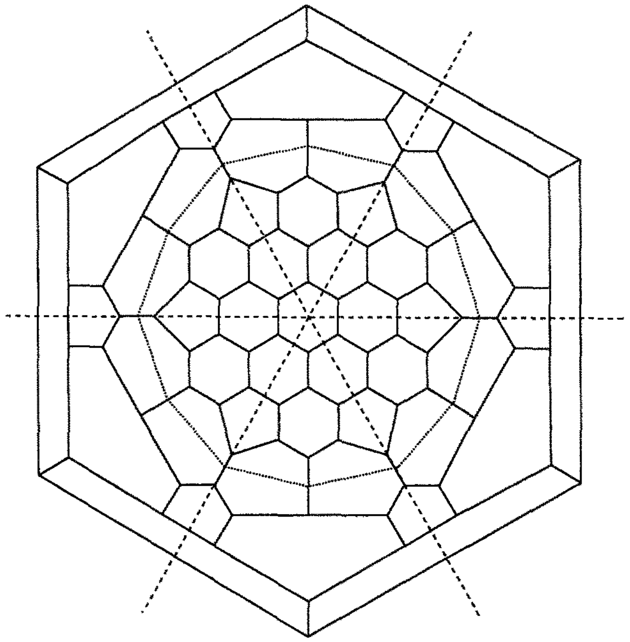

Fig. 6. Molecular graph for cluster **3**.

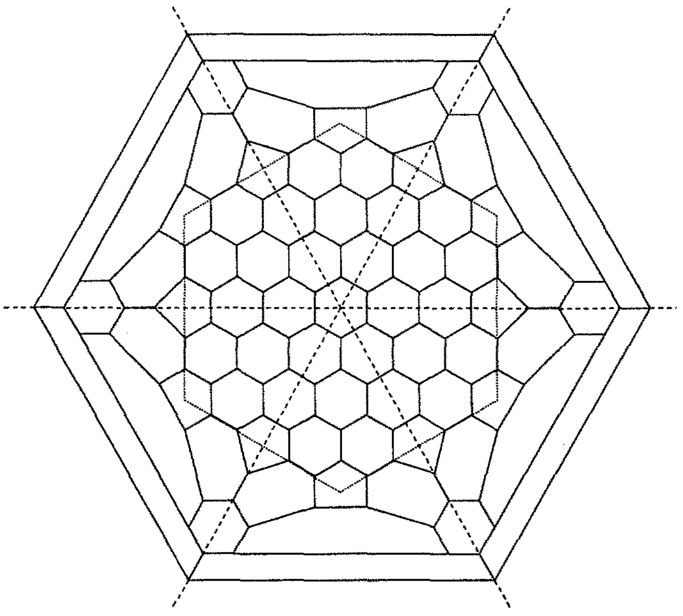

Fig. 7. Molecular graph for cluster **4**.

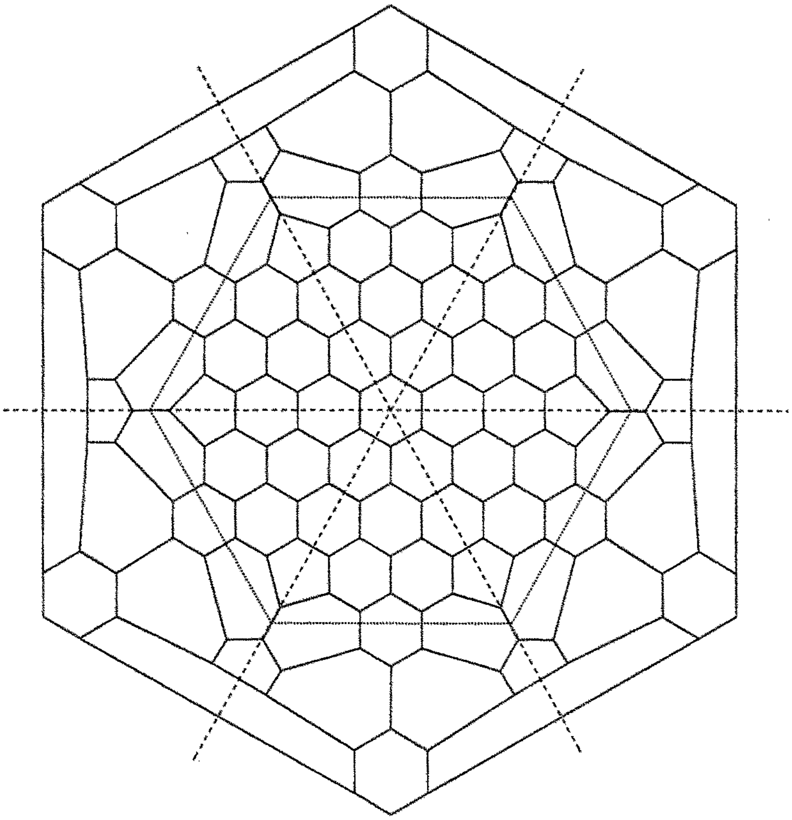

Fig. 8. Molecular graph for cluster **5**.

Flattened clusters with D_{6h} and D_{6d} symmetry

C_{72}-D_{6d}-f_1-*c* fullerene (1). The molecular graph for the polyhedral cluster **1** contains two coronenoid fragments f_1 (see Fig. 1), and the arrangement of pentagons corresponds to Scheme *c* (see Fig. 2). This molecular graph has 12 pentagonal and 26 hexagonal faces; the number of edges is equal to 108 (in Fig. 2 and hereinafter, the equator of the fullerene is indicated by a dotted line).

In the π-electron approximation, molecule **1** has a closed electron shell. The total π-electron energy (E_π), the delocalization energy (E_d), the energy of the highest occupied MO, and the degree of degeneracy of this MO as well as the energy gap (δ), which separates occupied and unoccupied MO levels, are given in Table 1. Note that a rather large value $\delta = 0.70|\beta|$ ($\beta \approx -2$ eV, the resonance integral) comparable to the energy gap for the C_{60} fullerene ($\delta = 0.75|\beta|$) corresponds to the C_{72} cluster.

Table 1. Results of calculations of C_n clusters by the Hückel method

Cluster	C_n	Symmetry	f_m	w	E_π	$E_d n^{-1}$	E_{HOMO}*	E_{LUMO}	δ
1	C_{72}	D_{6d}	f_1	*c*	112.07	0.557	0.564^2	−0.139	0.702
2	C_{96}	D_{6d}	f_1	*g*	148.86	0.530	0.378^2	0.378	0.000
3	C_{96}	D_{6h}	f_1	*a*	149.28	0.555	0.383^2	0.254	0.129
4	C_{144}	D_{6d}	f_2	*d*	225.38	0.565	0.432^2	−0.099	0.532
5	C_{180}	D_{6h}	f_2	*a*	282.05	0.567	0.374^2	−0.081	0.455
6	C_{180}	D_{6h}	f_2	*b*	281.55	0.564	0.279^2	0.186	0.093
7	C_{192}	D_{6d}	f_3	*e*	300.36	0.564	0.312^2	0.258	0.054
8	C_{108}	D_{3h}	f_1	*i*	168.72	0.566	0.466^2	−0.108	0.574
9	C_{144}	D_{3h}	f_1	*k*	224.70	0.560	0.353^2	−0.286	0.067
10	C_{162}	D_{3h}	f_2	*j*	253.75	0.566	0.402^2	−0.124	0.527
11	C_{216}	D_{3h}	f_3	*l*	337.99	0.565	0.259^2	0.259	0.000

Note. $E_d n^{-1}$ is the delocalization energy per electron, $\delta = |E_{HOMO} - E_{LUMO}|$ (in units of the resonance integral β); *w* is the type of arrangement of pentagons on the lateral surface of the polyhedron. * The upper index denotes the degree of degeneracy of the energy level.

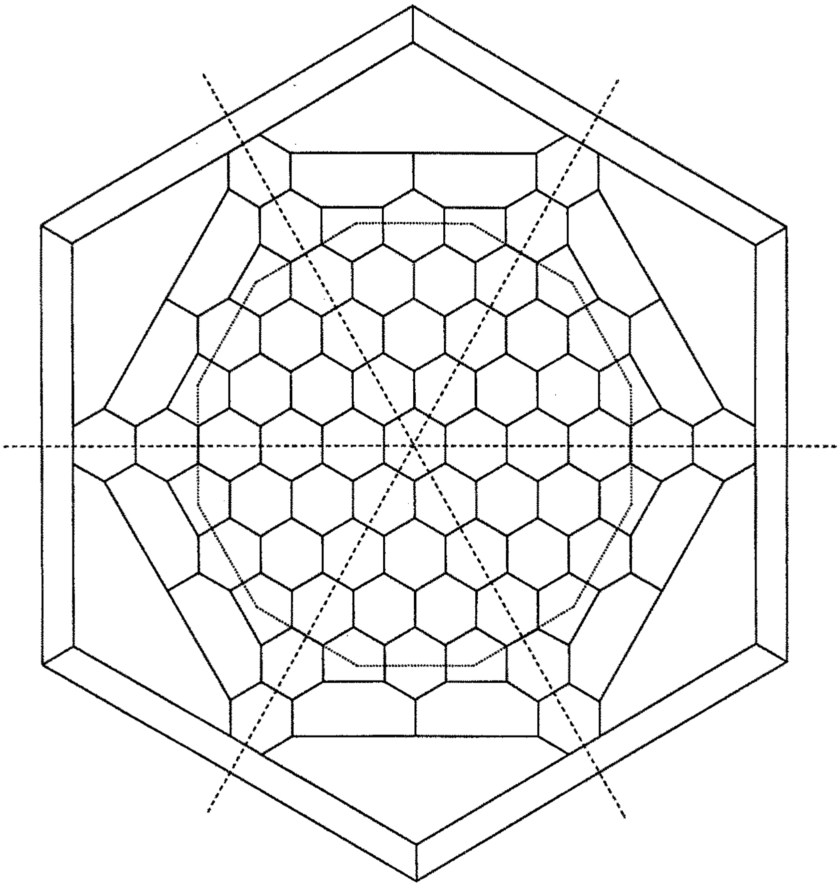

Fig. 9. Molecular graph for cluster **6**.

Molecule **1** has equivalent atoms of four types: Fig. 4 shows representatives of each type labeled by numbers 1—4. The π-electron densities (q_i) on atoms 1—4 are close to unity: q_1 = 0.979; q_2 = 1.016; q_3 = 1.00; and q_4 = 1.002. The differences in indices of free valence are more pronounced: the values are within the range 0.159—0.181. Therefore, the electron density distribution in cluster **1** is nearly uniform: the minimum electron density is located on atoms of type 1, while the maximum density is located on atoms of type 2. The bonds between atoms of pentagons, which are on the same side of the equatorial plane, have the largest order equal to 0.6; the bond 2—3 in the pentagon has the smallest order (0.476).

The results of calculations for the C_{72} cluster of the above-described topological structure performed by the MNDO, AM1, and MNDO/PM3 methods[17—19] with optimization of geometric parameters point to the presence of a local minimum on the potential energy surface of this cluster. Heats of formation ($\Delta_f H$), heats of formation per atom ($\Delta_f H n^{-1}$), ionization potentials (*IP*), and energy gaps (δ) obtained by the above-mentioned methods are given in Table 2.

The calculated values of the height (*H*) and diameter (*D*) of the C_{72} cluster depend only slightly on the method used and are within the ranges 5.74—5.86 Å and 8.33—8.41 Å, respectively.

C_{96} fullerenes. Schlegel diagrams for two isomers of C_{96} fullerene, which contain coronenoid fragments of type f_1, C_{96}-D_{6d}-f_1-g (**2**) and C_{96}-D_{6h}-f_1-a (**3**), are shown in Figs. 5 and 6, respectively. The arrangements of pentagons in cluster **2** and its analog **3** correspond to Schemes *g* and *a*, respectively (see Fig. 2). Isomer **2** can be obtained formally from cluster **3** by rotation of its lower portion by 30° with respect to the principal symmetry axis. Both polyhedral compounds contain 12 five-membered and 38 six-membered cycles and 144 C—C bonds each.

As is evident from the data in Table 1, molecule **3** has a lower π-electron energy compared to that of system **2**; molecule **3** has a quasi-closed shell (one bonding energy level is unoccupied). The electron shell of cluster **2** is open. The electron density distributions in isomers **2** and **3** are nearly uniform. In molecule **3**, the π-bond, which links pentagons, which are located on opposite sides of the equatorial plane, has the maximum order (0.623). The largest index of free valence (0.19) corresponds to peripheral atoms of coronenoid fragments.

The results of calculations for molecules **2** and **3** in the valence approximation by the MNDO, AM1, and

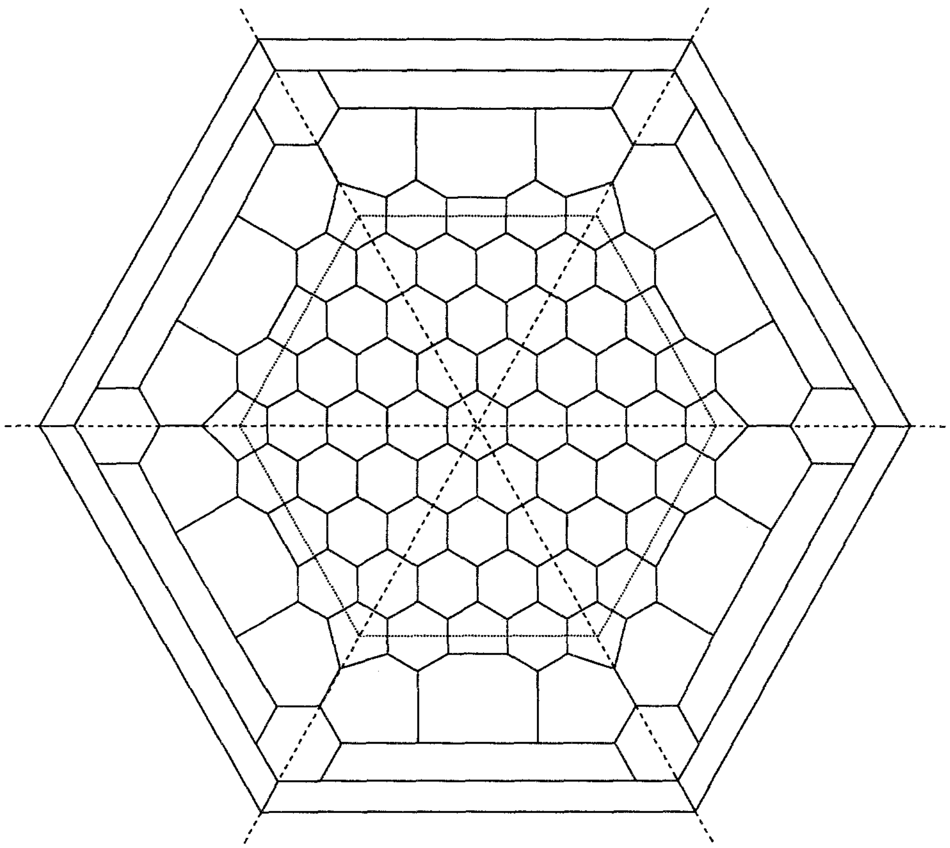

Fig. 10. Molecular graph for cluster **7**.

MNDO/PM3 methods with optimization of geometric parameters are given in Table 2. As is evident from the data in Table 2, cluster **3** (see also Ref. 20) should be substantially more stable than isomer **2** (the energies of these compounds differ by ~70 kcal mol^{-1}). However, this cluster is less stable (by ~30 kcal mol^{-1}) than the C_{96}-D_{6h}-f_1-h isomer, in which pentagons are linked according to Scheme *h* (see Fig. 2). The structure of this compound is close to spherical. It follows from the results of calculations that clusters **2** and **3** actually have a flattened shape, the values of the height (H = 6.7 Å) and diameter (D = 9.8 Å) are virtually independent of the method used.

Note that the C_{96}-D_{6d}-f_1-h cluster has been studied previously in the MNDO approximation.[21] An analysis of the results of our calculations (see also Ref. 21) demonstrates that the use of alternative parametrizations in the MNDO method only slightly affects the

Table 2. Energy and geometric characteristics of fullerenes C_n studied by the MNDO, AM1, and MNDO/PM3 methods

Cluster	C_n	Symmetry	Method	Heat of formation /kcal mol^{-1}		Energy characteristics/eV		Sizes/Å	
				$\Delta_f H$	$\Delta_f H n^{-1}$	IP	δ	H	D
1	C_{72}	D_{6d}	MNDO	985.0	13.68	8.91	6.30	5.864	8.409
			AM1	1111.0	15.42	9.40	6.39	5.748	8.354
			PM3	926.1	12.86	9.24	6.30	5.740	8.330
2	C_{96}	D_{6d}	MNDO	1197.4	12.47	8.03	3.43	6.706	9.866
			AM1	1375.1	14.32	8.52	3.37	6.598	9.975
			PM3	1148.5	11.96	8.47	3.55	6.591	9.758
3	C_{96}	D_{6h}	MNDO	1122.5	11.69	8.47	5.12	6.707	9.964
			AM1	1293.4	13.47	8.91	5.09	6.588	9.907
			PM3	1072.6	11.17	8.78	5.04	6.580	9.888

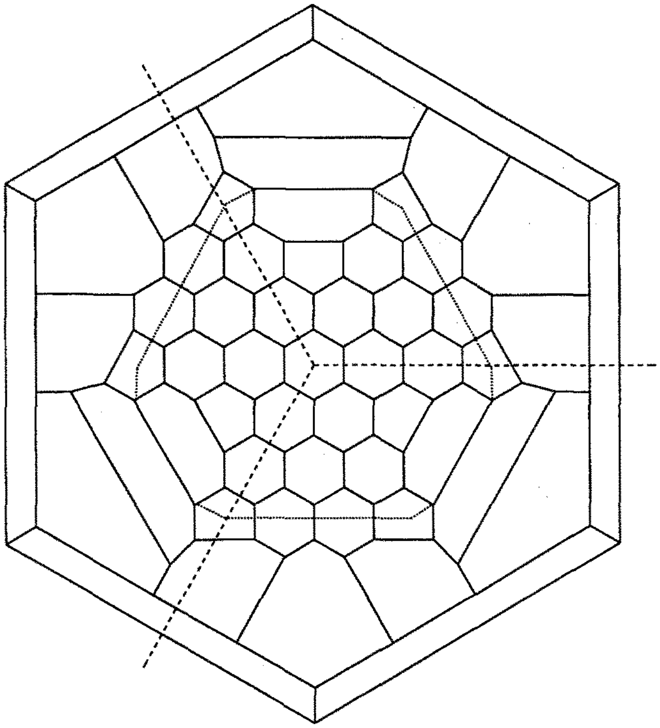

Fig. 11. Molecular graph for cluster **8**.

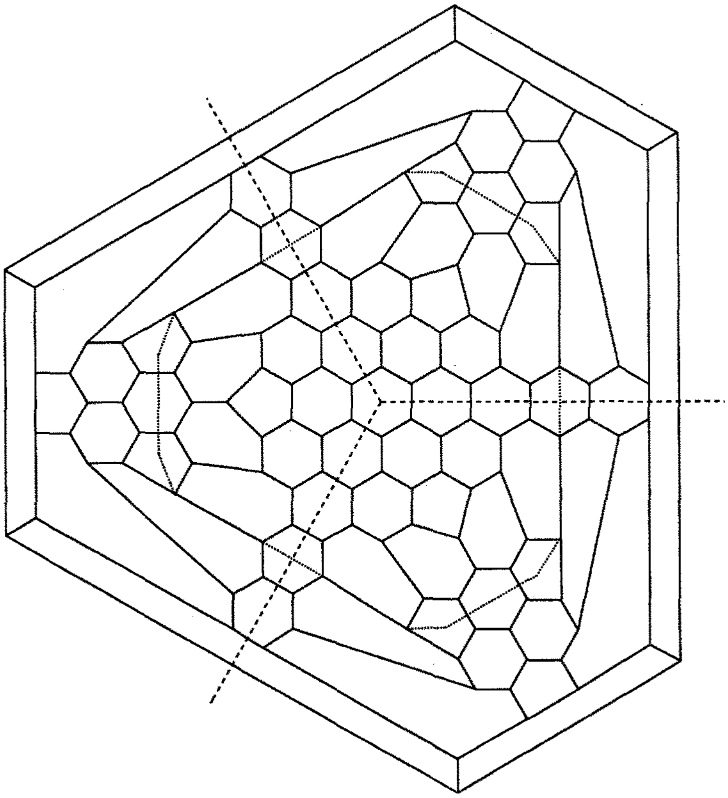

Fig. 12. Molecular graph for cluster **9**.

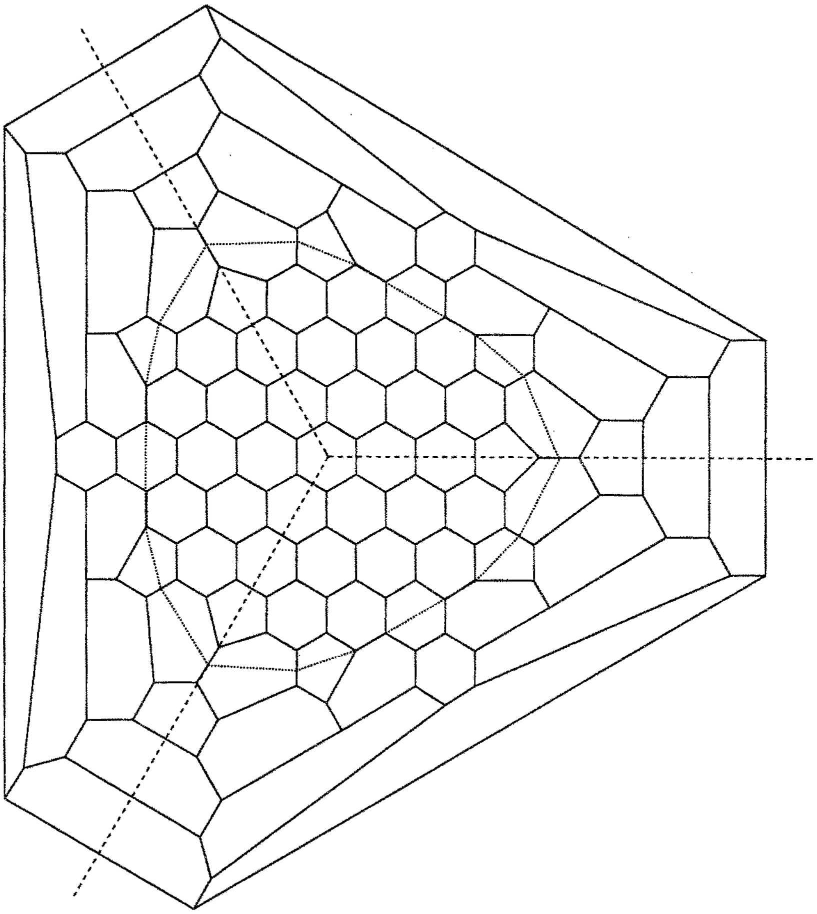

Fig. 13. Molecular graph for cluster **10**.

conclusions about the structure and stability of this cluster.

C_{144}-D_{6d}-f_2-*e* fullerene (4). Polyhedral molecule **4** can be conceived as a combination of two fragments f_2 of a graphite layer, each consisting of 54 atoms, and a system of polycondensed five- and six-membered carbon cycles with the arrangement of pentagons according to Scheme *e* (see Fig. 2). The carbon framework of cluster **4** is described by the molecular graph, which contains 12 pentagons, 62 hexagons, and 216 edges (see Fig. 7). Molecule **4** has a closed electron shell in the π-electron approximation. The delocalization energy for cluster **4** is higher than that for C_{60}-I_h fullerene, while the energy gap ($\delta = 0.532|\beta|$) is rather large (see Table 1).

The π-electron density distribution in molecule **4** is nearly uniform: π-populations of atoms vary from 0.975 to 1.027, while the indices of free valence are in the range from 0.158 to 0.181. The π-bonds, which link atoms of adjacent pentagons located on the same side of the equator, have the maximum orders equal to 0.580.

C_{180} fullerenes. The molecular graphs for two isomers of the C_{180} fullerene with D_{6h} symmetry, which contain coronenoid fragments f_2 (as in molecule **4**), C_{180}-D_{6h}-f_2-*a* (**5**) and C_{180}-D_{6h}-f_2-*b* (**6**), are shown in Figs. 8 and 9, respectively. Both compounds contain 12 five-membered and 80 six-membered cycles as well as 270 C—C bonds. Molecule **5** has a closed electron shell and a rather high delocalization energy (see Table 1). In isomer **6**, the electron shell is quasi-closed. The π-electron system of cluster **5** is more stable than that of its analog **6**. Moreover, the energy gap δ in molecule **6** is smaller than that in isomer **5**. The electron density distributions in these clusters are nearly uniform. The bonds between adjacent pentagons have the maximum π-order equal to ~0.85.

C_{192}-D_{6d}-f_3-*e* fullerene (7). The molecular graph for cluster **7** is shown in Fig. 10. This cluster contains 12 pentagons, 86 hexagons, and 288 edges; the structure of this cluster can be described in terms of two coronenoid fragments f_3 joined together; each of these fragments consists of 96 atoms. These fragments are arranged one above the other; the upper layer is rotated with respect to the lower layer by 30°. In this case, the arrangement of pentagonal faces corresponds to Scheme *e* (see Fig. 2). The electron shell of fullerene **7** is quasi-closed, the

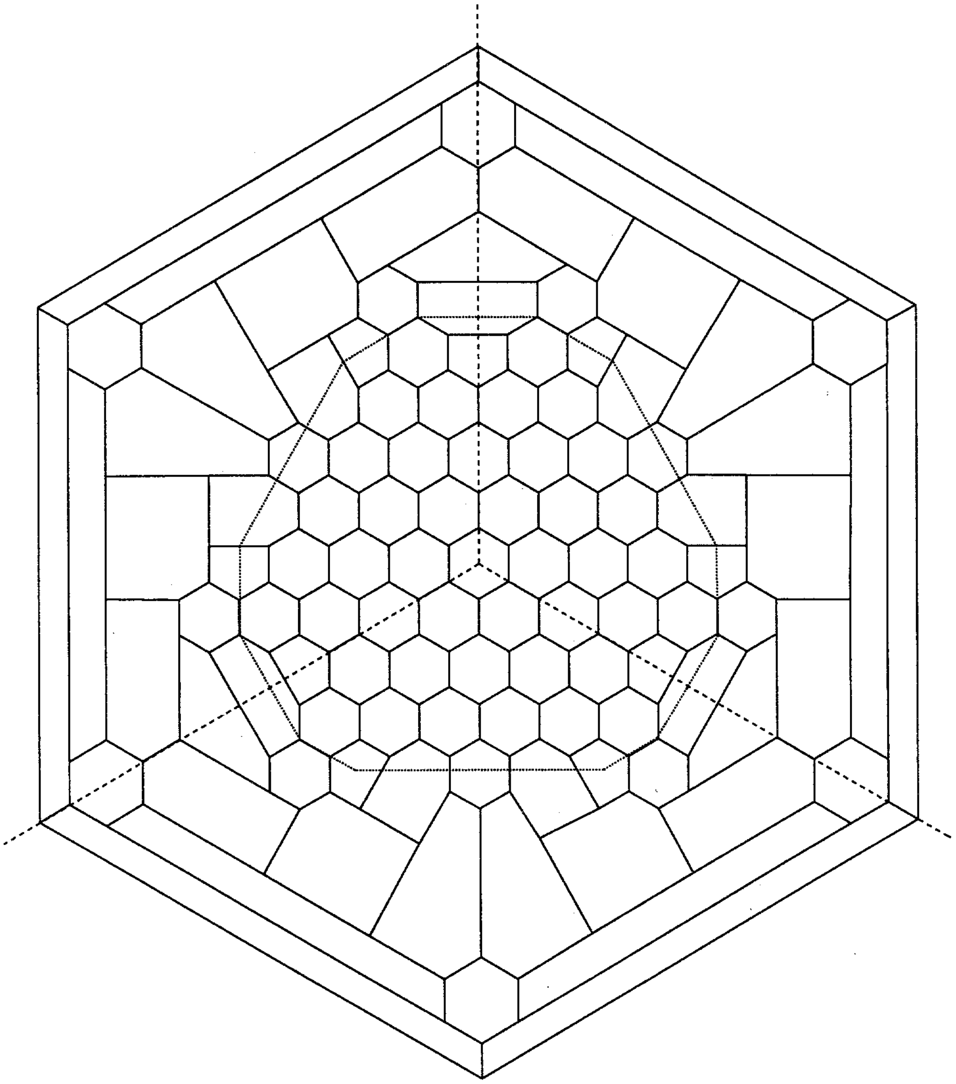

Fig. 14. Molecular graph for cluster **11**.

energy gap δ is small (see Table 1) while the delocalization energy is rather high.

Flattened clusters with D_{3h} symmetry

C_{108}-D_{3h}-f_1-*i* fullerene (8). The molecular graph for molecule **8** is shown in Fig. 11. The corresponding polyhedron contains 12 five-membered and 44 six-membered cycles as well as 162 C—C bonds. The π-electron system of molecule **8** has a closed shell, a high delocalization energy, and a nonzero energy gap δ (see Table 1). The electron density distribution is nearly uniform. The orders of the bonds linking adjacent pentagons are the largest.

C_{144}-D_{3h}-f_1-*k* fullerene (9). The molecular graph for molecule **9** (see Fig. 12) contains 12 pentagons, 62 hexagons, and 216 edges; the π-electron shell of molecule **9** is quasi-closed; the energy gap is close to zero (see Table 1). The electron density on atoms ranges from 0.969 to 1.056. The minimum order of π bonds is 0.462, while the maximum order is 0.582. The topological distance between atoms of pentagons is equal to two.

C_{162}-D_{3h}-f_2-*j* fullerene (10). The molecular graph for cluster **10** is shown in Fig. 13 and contains 12 pentagons, 71 hexagons, and 243 edges. The π-electron system of molecule **10** has a closed shell. The electron density on atoms varies from 0.978 to 1.035. The orders of bonds are in the range from 0.477 to 0.597. The indices of free valence vary in the range 0.16—0.18.

C_{216}-D_{3h}-f_3-*l* fullerene (11). The molecular graph for molecule **11** is shown in Fig. 14 and contains 12 pentagons, 98 hexagons, and 324 edges. The π-electron system of molecule **11** has an open shell. The electron density on atoms ranges from 0.959 to 1.065.

Results and Discussion

It follows from the preceding that among the studied complexes **1**—**11**, which can be formally described as cross-linked fragments of graphite layers of the coronenoid type, the systems (**1**, **9**, **4**, **10**, and **5**) with closed π-electron shells (see Table 1) exist. Four more compounds have quasi-closed shells, and only two of 11 studied clusters (**2** and **11**) have open shells. Note that in the valence approximation, a local minimum was found on the potential energy surface of cluster **2**; the structure with the closed electron shell corresponds to this minimum. For the studied systems, the average value of the delocalization energy (E_dn^{-1}) is close to the analogous value for C_{60}-I_h fullerene (0.557|β|). It should be particularly mentioned that cluster **7** is a combination of two coronenoid fragments f_3; all 12 pentagonal faces are obtained automatically (without addition of a lateral surface) and are separated by C—C—C linear bridges (see Fig. 2, Scheme *e*).

The above-mentioned method of generation of flattened clusters with D_{6h} and D_{6d} symmetry allows the extension to systems with a rather large number of atoms. As a result, the molecular graphs for the C_n-D_{6h}-f_m-a and C_n-D_{6h}-f_m-b compounds, which contain identical coronenoid fragments f_m but differ in the mutual arrangement of five-membered cycles, can be constructed. The molecular graphs for the flattened fullerenes with D_{6d} symmetry are formed by rotation of one of the coronenoid fragments in the corresponding cluster with D_{6h} symmetry by some angle, which is determined by sizes of these fragments.

Clusters with D_{3h} symmetry are constructed in the same manner as described for systems with D_{6h} symmetry. Apparently, the diameter of a polyhedron increases while the height tends to the finite limit (*i.e.*, $H \ll D$) with increasing degree of extension of the coronenoid fragment; these structures are quasi-two-dimensional. Estimations of heights of the studied clusters, which were performed using the C_{96} molecule as an example, demonstrated that the distance between coronenoid fragments f_m is approximately twice as large as the distance between layers in graphite. Therefore, the results of calculations provide evidence that along with quasi-one-dimensional forms of carbon, namely, tubulenes (molecular wires), quasi-two-dimensional forms of carbon are also possible.

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References

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smally, *Nature*, 1958, **318**, 162.
2. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature*, 1990, **347**, 354.
3. M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *J. Mater. Res.*, 1993, **8**, 2054.
4. V. I. Sokolov and I. V. Stankevich, *Usp. Khim.*, 1993, **62**, 455 [*Russ. Chem. Rev.*, 1993, **62**, 419 (Engl. Transl.)].
5. S. Iijima, *Nature*, 1991, **354**, 56.
6. D. Ugarte, *Nature*, 1992, **359**, 707.
7. D. Bakowies and W. Thiel, *J. Am. Chem. Soc.*, 1991, **113**, 3705.
8. L. A. Chernozatonskii, *Phys. Rev. Lett.*, 1991, A**160**, 392.
9. L. A. Chernozatonskii, *Phys. Rev. Lett.*, 1992, A**172**, 173.
10. M. Fujita, M. Yoshida, and E. Osawa, *Fullerene Sci. Technol.*, 1995, **3**, 93.
11. P. W. Fowler, J. E. Cremona, and J. I. Steer, *Theor. Chim. Acta*, 1988, **73**, 1.
12. T. J. Schmalz, W. A. Seitz, D. J. Klein, and G. E. Hite, *J. Am. Chem. Soc.*, 1988, **110**, 1113.
13. E. G. Gal'pern, I. V. Stankevich, A. L. Chistyakov, and L. A. Chernozatonskii, *Pis'ma v ZhETF*, 1992, **55**, 469 [*JETP Lett.*, 1992, **55**, 483 (Engl. Transl.)].
14. E. G. Gal'pern, I. V. Stankevich, A. L. Chistyakov, and L. A. Chernozatonskii, *Fullerene Sci. Technol.*, 1994, **2**, 1.
15. E. C. Kirby, *Fullerene Sci. Technol.*, 1994, **2**, 405.
16. T. Pisanski, A. Zitnik, A. Graovac, and A. Baumgartner, *J. Chem. Inf. Comp. Sci.*, 1994, **34**, 1090.
17. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.
18. T. Clark, *A Handbook of Computational Chemistry*, John Wiley and Sons, New York, 1985.
19. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209.
20. I. V. Stankevich and A. L. Chistyakov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, **44**, 629 [*Russ. Chem. Bull.*, 1995, **44**, 608 (Engl. Transl.)].
21. R. L. Murry and G. E. Scuseria, *J. Phys. Chem.*, 1994, **98**, 4212.

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