D_{6h}—C_{96} fullerene

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The possibility of the existence of a polyhedral C_{96} cluster with D_{6h} symmetry, composed of 12 pentagonal and 38 hexagonal faces, has been estimated. Minima on the potential energy surface of the singlet state of this cluster were found, optimized geometry was determined, and the electronic structure was studied by the MNDO/PM3 and AM1 methods.

Key words: fullerenes, polyhedral carbon clusters, MNDO/PM3 and AM1 methods.

Polyhedral carbon clusters, fullerenes, with a large number of atoms (up to several hundreds) are produced by vaporizing graphite or by subjecting graphite to an electron beam with sufficiently high energy.[1–3] However, structural studies of such large systems by X-ray structural analysis are hampered because the required compound is difficult to produce in macroquantities, and crystals of sufficiently large dimensions are difficult to obtain. Moreover, it should be mentioned that even when $n = 60$ all polyhedral carbon clusters can have a substantial number of isomers. Therefore, calculational methods, and specifically quantum-chemical methods capable of predicting the structure and different energy characteristics of molecules yet to be synthesized, are of particular importance for these systems.[4–6]

Clusters containing over 70 carbon atoms are generally classified as higher fullerenes. These fullerenes must contain fairly large extended fragments in the form of pericondensed six-membered cycles, which can be considered as a part of a graphite layer. These fragments are also observed in the C_{70} cluster.

In principle, the possibility cannot be excluded that under specific extreme conditions, two relatively small fragments of a graphite layer occur, cross-linking of which affords polyhedral structures. In this work, we discuss the results of quantum-chemical calculations for one of the clusters of this type, namely, the D_{6h}—C_{96} cluster (**1**) with D_{6h} symmetry. The Schlegel diagram of this cluster is given in Fig. 1.

The polyhedron describing the σ network of cluster **1** has 96 vertices, 144 edges, 12 pentagonal faces, and 38 hexagonal faces. Clusters consisting of 24 carbon atoms are disposed at the poles of the molecule under study. The σ network of each of these clusters is topologically equivalent to the carbon network of the coronene molecule. The polycyclic structure with D_{6h} symmetry (consisting of 48 carbon atoms), which contains 24 hexagonal and 12 pentagonal faces, is located between these coronene fragments. The set of 12 pentagons is subdivided into 6 pairs. The pentagons of each pair are linked to each other *via* shared edges (similarly to torelenes[7]).

Calculations for molecule **1** were performed using three quantum-chemical methods: in the π-electron

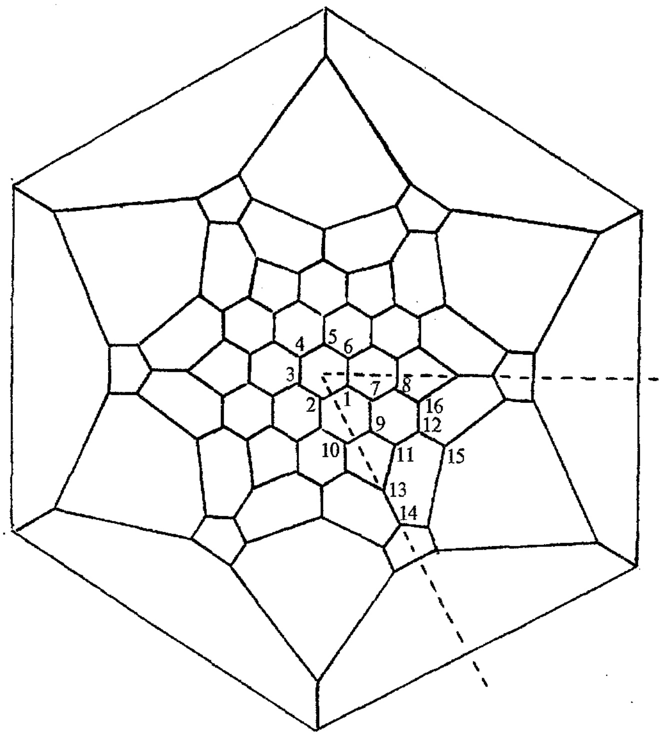

Fig. 1. Planar molecular graph (the Schlegel diagram) for the D_{6h}—C_{96} cluster. The repeating unit is marked by dashed lines.

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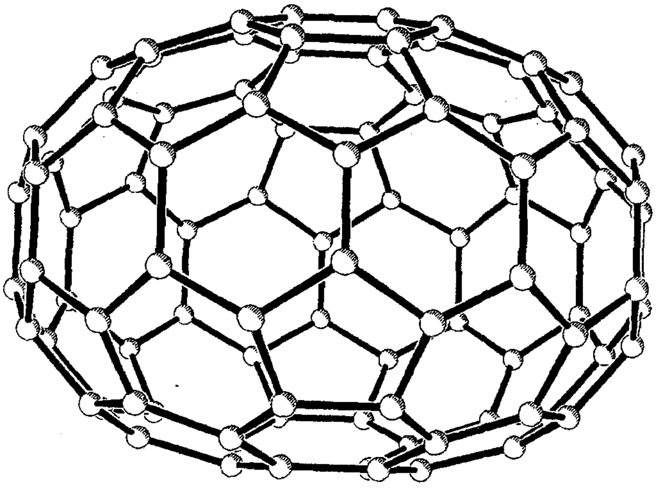

Fig. 2. The geometry of the D_{6h}—C_{96} cluster obtained by full energy optimization in the valence approximation MNDO/PM3 (computer graphics).

approximation by the Hückel method on a PC AT/486 computer and in the valence approximation by the AM1 and MNDO/PM3 methods on an Alpha-5 computer.

The π-electron approximation. It was established by the Hückel method that the π-electron shell of molecule **1** is quasi-closed; the highest occupied energy level ($E_{\text{HOMO}} = 0.38\beta$, where β is the resonance integral) is doubly degenerate and filled by four electrons. The lowest unoccupied energy level is located in the bonding region of the spectrum. The width of the energy gap separating occupied and unoccupied levels is $0.13|\beta|$. Delocalization energy per electron (0.550β) is close to that of the C_{60} fullerene molecule (0.553β).[8]

The valence approximation. The geometric and electronic structure of polyhedral cluster **1** was studied in more detail by the MNDO/PM3 and AM1 methods. Energy optimization of 14 independent geometric parameters for the singlet state of molecule **1** with retention of D_{6h} symmetry reveals the existence of a local minimum on the potential energy surface. When choosing the initial approximation for the structure of **1**, the coronene fragments were assumed to be planar.

Energy optimization demonstrated that the polar caps of the polyhedra are convex (Fig. 2). The distance between the two planes in which the inner and peripheral atoms of the coronene fragment are located, is 0.822 Å (PM3) or 0.816 Å (AM1). The angle between the C(1)—C(7) bond (see Fig. 1) and the plane of the C(1)···C(6) face is close to 15° (PM3, AM1).

Therefore, cluster **1** has the shape of a flattened sphere. The dimensions of this cluster (in Å) are as follows: the height is 6.580 (PM3) or 6.588 (AM1); the diameter is 9.888 (PM3) or 9.907 (AM1). In cluster **1**, 6 different types of equivalent atoms are present. Figure 1 shows representatives of each type labeled by the numbers 1, 7, 8, 11, 12, and 13.

Table 1. Bond lengths (*d*) and their indices (according to Wiberg[9]) of the D_{6h}—C_{96} cluster calculated by the MNDO/PM3 and AM1 methods

Bond*	d/Å		Bond index/au	
	PM3	AM1	PM3	AM1
1—2	1.429	1.433	1.312	1.300
1—7	1.469	1.467	1.094	1.088
7—9	1.404	1.406	1.321	1.311
9—10	1.448	1.451	1.075	1.067
9—11	1.425	1.434	1.315	1.303
11—12	1.410	1.412	1.309	1.302
11—13	1.461	1.465	1.075	1.065
12—15	1.460	1.462	1.113	1.100
13—14	1.367	1.368	1.576	1.573

* Atomic numbering scheme is shown in Fig. 1.

The bond lengths in molecule **1** are shorter than the single C—C bond length (Table 1). The *exo* bonds between the atoms of the pentagons are shorter (larger Wiberg[9] bond indices correspond to these bonds). The C(1)—C(7) bond and symmetrically equivalent bonds are the longest. The bond lengths in the pentagons are in the range 1.425—1.461 Å.

The bond angles at the C atoms in most of the hexagons are close to 120°. The most substantial deviations were found for atom 7 and equivalent atoms (the C(8)—C(7)—C(9) angle is 113°; the C(11)—C(12)—C(16) angle is 115°). The bond angles in the pentagons are 108.0 ± 0.7°.

Note that the scheme of energy levels of the frontier molecular orbitals in the valence approximation is qualitatively identical to that obtained by the Hückel method: the highest occupied level is doubly degenerate and complete ($E_{\text{HOMO}} = -8.8$ eV (PM3) and -8.9 eV (AM1)), while the lowest unoccupied level is nondegenerate. The heat of formation per atom of cluster **1** (kcal mol^{-1}) is 11.1 (PM3) or 13.5 (AM1), *i.e.*, it is smaller than that for the I_h—C_{60} cluster (13.5 or 16.2, respectively). The difference in energies of LUMO and HOMO is rather large (5.0 (PM3) and 5.1 eV (AM1)), which should enhance the kinetic stability of cluster **1** (for I_h—C_{60} fullerene, the corresponding values are 8.8 and 8.9 eV, respectively). The results of calculations also demonstrate that the value of the first ionization potential should be smaller than that for cluster I_h—C_{60} by approximately 0.7 eV (the experimental value[5] is 6.4—7.9 eV). Therefore, the above-mentioned characteristics favor the stability of the studied cluster D_{6h}—C_{96}.

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References

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature,* 1985, **318**, 161.
2. H. W. So and C. L. Wilkins, *J. Phys. Chem.*, 1989, **93**, 1184.
3. D. Ugarte, *Nature,* 1992, **359**, 707.
4. V. I. Sokolov and I. V. Stankevich, *Usp. Khim.*, 1993, **62**, 455 [*Russ. Chem. Rev.*, 1993, **62** (Engl. Transl.)].
5. D. Bakowies and W. Thiel, *J. Am. Chem. Soc.,* 1991, **113**, 3704.
6. D. Bakowies and W. Thiel, *Chem. Phys.*, 1991, **151**, 309.
7. E. G. Gal'pern, I. V. Stankevich, A. L. Chistyakov, and L. A. Chernozatonskii, *Fullerene Science and Technology,* 1994, **2**, 1—11.
8. D. A. Bochvar and E. G. Gal'pern, *Dokl. Akad. Nauk SSSR,* 1973, **209**, 610 [*Dokl. Chem.*, 1973, **209** (Engl. Transl.)].
9. K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083.

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