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TORELENES (t)-C_n AS A NEW CLASS OF CARBON CLUSTERS. ELECTRONIC STRUCTURE OF (t)-C_{200}, (t)-C_{210}, (t)-C_{276}, AND (t)-C_{408}.

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Abstract

Structures of four giant torus-like carbon clusters are proposed: (t)-C_{200} (I), (t)-C_{210} (II), (t)-C_{408} (III) and (t)-C_{276} (IY). Their electronic structures are calculated by a topological approach. It is discovered that electronic shell of cluster (II) containing $(4n+2)$ π-electrons with $n = 52$ is closed. Its spectrum gap is equal to 0.4. (In units of resonance integral β module.) Clusters (I), (III) and (IY) belong to conjugated systems containing $4n$ π–electrons. The first one has an open electronic shell and is inclined to dianion formation. Clusters (III) and (IY) possess pseudo-closed electronic shells, their spectrum gaps are equal to 0.14 and 0.08, respectively.

Introduction

Several new molecular types of allotropic carbon forms have been obtained lately [1,2]. The new carbon forms consist of finite size clusters, usually called fullerenes.

Fullerenes have forms of convex polyhedra. Their faces are formed by pentagons and hexagons. Clusters I_h-C_{60} and D_{5h}-C_{70} are the most available and investigated ones nowadays. Beside sphere-like carbon molecules, cylinder-like (barrelenes and capsulenes) and bulb-like forms are discussed in literature [3-8]. In paper [9] it has been noted that under definite conditions carbon network fragments covering a negative curvature surface can be obtained.

Polyhedron-type finite carbon clusters known nowadays belong to one and the same class of carbopolyhedra. As polyhedron and sphere are diffeomeomorphic, it is natural to call such carbon clusters genre-0 clusters. In paper[10] it was proposed that besides convex polyhedral forms toroidal carbon molecules may exist. The σ-bonds of these molecules form a degree 3 homogenious network that covers a torus. From topological point of view the torus is a genre-1 surface as it is homeomorphic to a sphere with a handle.

It is necessary to note that torus-like systems covered by a hexagonal network were discussed in 1954 already by Heilbronner[11]. However, a hexagonal network covering a relatively small size torus can hardly be an adequate model of a torus-like carbon cluster. Such net should be greatly distorted, especially on the inner part of the torus. Note that Euler formula for a toroid carbon cluster is as follows [12]: $V - E + F = 0$. The values of V, E and F are equal to the number of atoms, σ-bonds and simple cycles, respectively. Let F_j be the number of j-membered rings. In the case of a homogeneous 3-d degree network that are generated by sp^2-hybridized carbon atoms on the torus these numbers are bound by the equation:

$$F_3 + 2F_4 + F_5 - F_7 - 2F_8 - 3F_9 - 4F_{10} -...= 0.$$

The formula means that a torus-like cluster including pentagons inevitably includes simple cycles with more than 6 atoms. For geometry reasons, a tore covered by nets of pentagons, hexagons and octagons is the most appropriate model for toroidal carbon cluster. Pentagons are placed at the outer torus surface, while in "bath"-conformation octagons are situated at the inner torus surface[10]. It follows from the Euler formula that

$F_5 = 2F_8$. On the base of this relation it is possible to construct carbotoroid models of D_{5h} and D_{6h} symmetry. In the paper we correspond results of investigations of four representatives of such genre-1 carbon clusters. These are toroidal clusters (t)-D_{5h}-C_{200} (I) and (t)-D_{5h}-C_{210}(II), (t)-D_{6h}-C_{408}(III) and (t)-D_{6h}-C_{276} (IY) possessing 5-th and 6-th order symmetry axes. Repeating fragments of clusters I - IY are presented in figures (I) - (4). Fig. 5 depicts a model of cluster (IY). Electronic structure calculations of clusters are fulfilled in topological approximation by the Huckel method. By analogy with genre-0 carbon clusters we suppose that all Coulomb integrals don't depend on the position of carbon atoms ($\alpha_j=\alpha$) and all resonance integrals are equal to one and the same value β .

1. Carbo-toroid (t)-D_{5h}-C_{200} (I).

Such carbon cluster consists of 10 pentagons, 5 octagons and 85 hexagons. Molecular graph of a repeating fragment of cluster (I) is shown in Fig. 1. The calculation proves that toroid (t)-C_{200} has 101 bonding energy levels. The highest of them has double degeneration and is equal to $\alpha+0.12\beta$. The lowest occupied energy level is equal to $\alpha+3.0\beta$. Bonding energy levels are situated in the interval [$\alpha + 0.12\beta$, $\alpha + 3.0\beta$]. The ground state of cluster (I) is to be paramagnetic. The cluster should be also apt to dianion formation. The lowest unoccupied energy level lies in the anti-bonding domain of one-electron energy levels and is equal to $\alpha - 0.039\beta$. The gap width between the occupied energy levels in the ground state and the vacant ones is equal to -0.16β. As a whole, the spectrum character of a (t)-C_{200} cluster is like that of a graphite layer which is usually calculated under periodic boundary conditions for a wave function.

Analysis of electronic charge density q_j at atoms in a dianion of (I) shows that it is practically independent of carbon atom positions on the torus, $q_j = 1.000 \pm 0.006$ a.u. Maximum electronic density is concentrated at pentagons' atoms. This corresponds to acceptor properties of a cyclopentadienyl radical. The bond joining two pentagons has

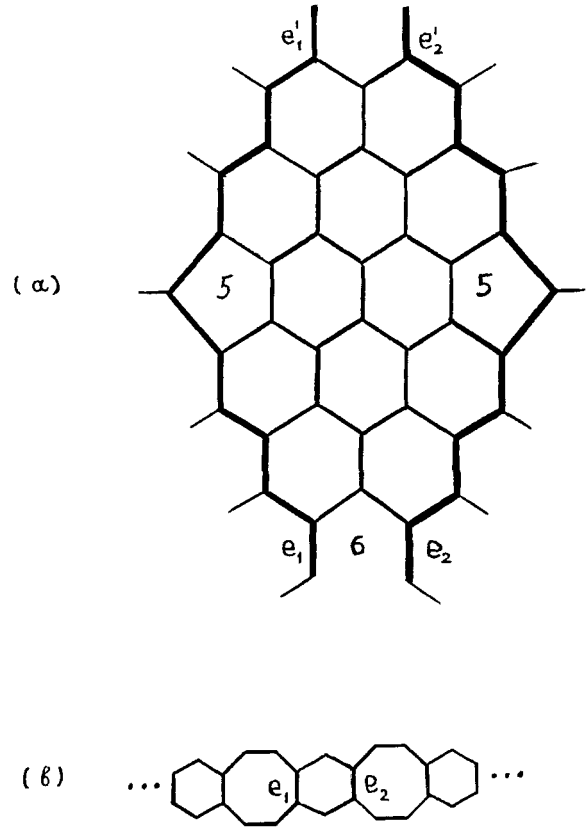

Fig. 1. (a) - The molecular graph of a repeating fragment of a toroid carbon cluster (t)-D_{5h}-C_{200} (I). Bold line is the boundary of this graph. The edges marked by symbol $\mathbf{e}_i$ and $\mathbf{e}_i'$ (as well $\mathbf{e}_2$ and $\mathbf{e}_2'$) must be identified. (b) - Structure of tore (I) fragment inner part.

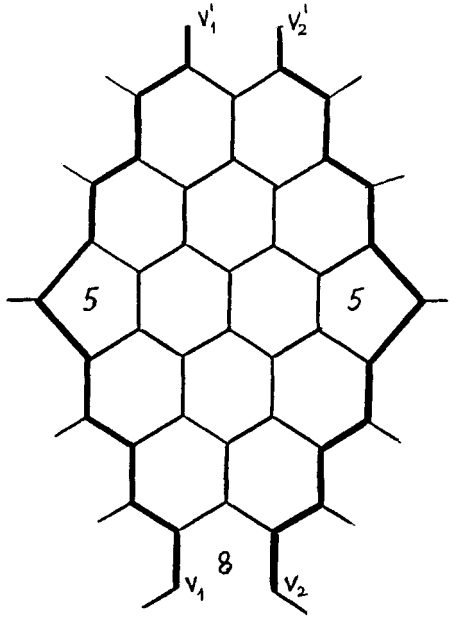

Fig. 2. The molecular graph of a repeating fragment of a toroid cluster (t)-D_{5h}-C_{210} (II). Bold line is the boundary of this graph. The atoms (vertices) marked by symbols $\mathbf{v}_1$ and $\mathbf{v}_1'$ (as well $\mathbf{v}_2$ and $\mathbf{v}_2'$) must be identified.

bond order equal to 0.572. Bond orders in pentagons are equal to 0.489. Note also that the greatest index of a free valence is equal to 0.19. These values correspond to atoms situated in the inner part of the torus. The atoms may have large affinity to addition of a radical particle.

2. Carbo-toroid (t)-D_{5h}-C_{210} (II).

There are ten pentagons, five octagons and 90 hexagons in this carbon molecule. A molecular graph describing bonding topology in a repeating fragment is presented in Fig. 2. Cluster (II) has a closed electron shell and a sufficiently large one-electron spectrum

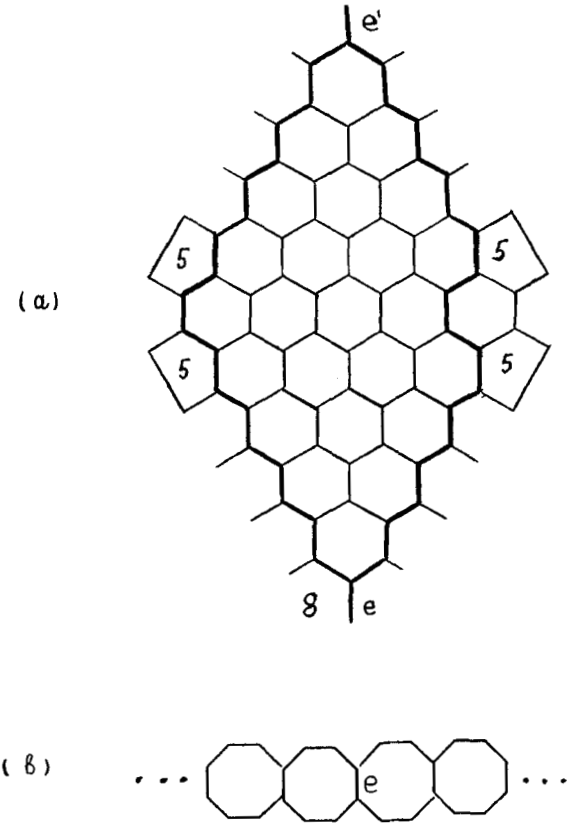

Fig. 3. (a) - The molecular graph of a repeating fragment of a toroid carbon cluster (t)-D_{6h}-C_{408} (III). Bold line is the boundary of this graph. The edges marked by symbols **e** and **e'** must be identified. (b) - Structure of tore (III) fragment inner part.

gap that is equal to -0.42β. Analysis of electronic charge density at the atoms proves that the value is almost evenly distributed and is changed in the interval 1.00 ± 0.03 a.u. Maximum of electronic density is localized at carbon atoms situated on the most distant from the torus symmetry axis positions. Bond orders are in the interval from 0.48 (in octagons) to 0.56. Bond orders in pentagons are equal to about 0.5. Hexagons are

Table. Energy of the lowest unoccupied molecular orbital $\alpha+\beta\ x_{LUMO}$ and highest occupied one $\alpha+\beta\ x_{HOMO}$, gap $\Delta\varepsilon$ (in units $-\beta$) for carbo-toroids (I) - (IY) and I_h-C_{60} fullerene.

	C_{200}	C_{210}	C_{408}	C_{276}	C_{60}
x_{LUMO}	-0.039	-0.065	0.085	0.073	-0.138
x_{HOMO}	0.144*	0.359	0.226	0.084*	0.616
$\Delta\varepsilon$	0.160	0.424	0.141	0.011	0.750

* This energy level is double degenerated and there are only two electrons at it.

divided into two types: with equal bond orders (aromatic cycles) and alternating ones. The difference between these bond orders is equal to 0.05.

3. Carbo-toroid (t)-D_{6h}-C_{408} (III).

There are twelve pentagons, six octagons and 198 hexagons in this carbon molecule. A molecular graph describing the σ -skeleton of a repeating fragment of cluster (III) is presented in Fig. 3. Cluster (III) has a pseudo-closed electronic shell as the lowest unoccupied energy level is situated in the bonding region of spectrum (see Table). Electronic charge densities at atoms are about 1 a.u., while bond orders vary in the interval from 0.42 to 0.55. The cluster may have large electron affinity.

4. Carbo-toroid (t)-D_{6h}-C_{276} (IV).

A molecular graph describing the σ-skeleton of a repeating fragment of cluster (IV) is presented in Fig. 4. The cluster consists of 104 hexagons, 12 pentagons and 12 heptagons (see also Fig.5). Cluster (IV) has a non-closed electronic shell as its highest occupied energy level (α + 0.084β) has double degeneration and is occupied by two electrons. Besides, there is another empty bonding energy level that is equal to α +

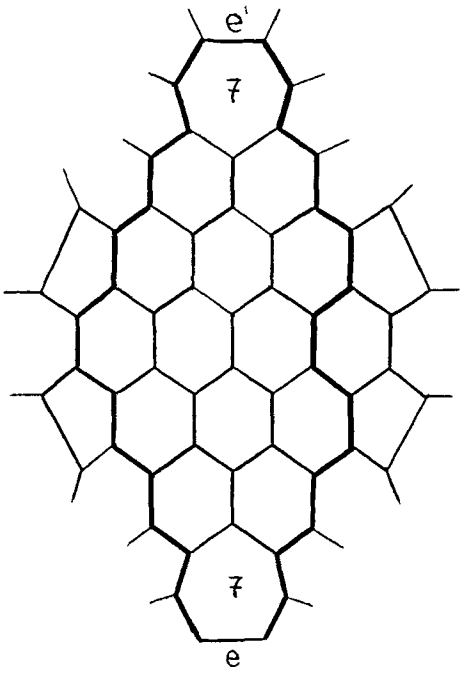

Fig. 4. The molecular graph of a repeating fragment of toroid-like carbon cluster (t)-D_{6h}-C_{276} (IY): Bold line is the boundary of this graph. The edges **e** and **e'** must be identified.

0.073β. The ground state of cluster (IV) is to be paramagnetic. The anionic forms of the cluster may have multiplicity equal to 4.

5. Results discussion.

Cluster (II) can be classified as a conjugated system that contains (4n + 2) π-electrons, with n = 52. It follows from our calculations (see Table) that this molecule has a closed electronic shell and a sufficiently large gap, which can provide kinetic stability of the cluster. Using numerical values of parameters, defined on the base of experimental

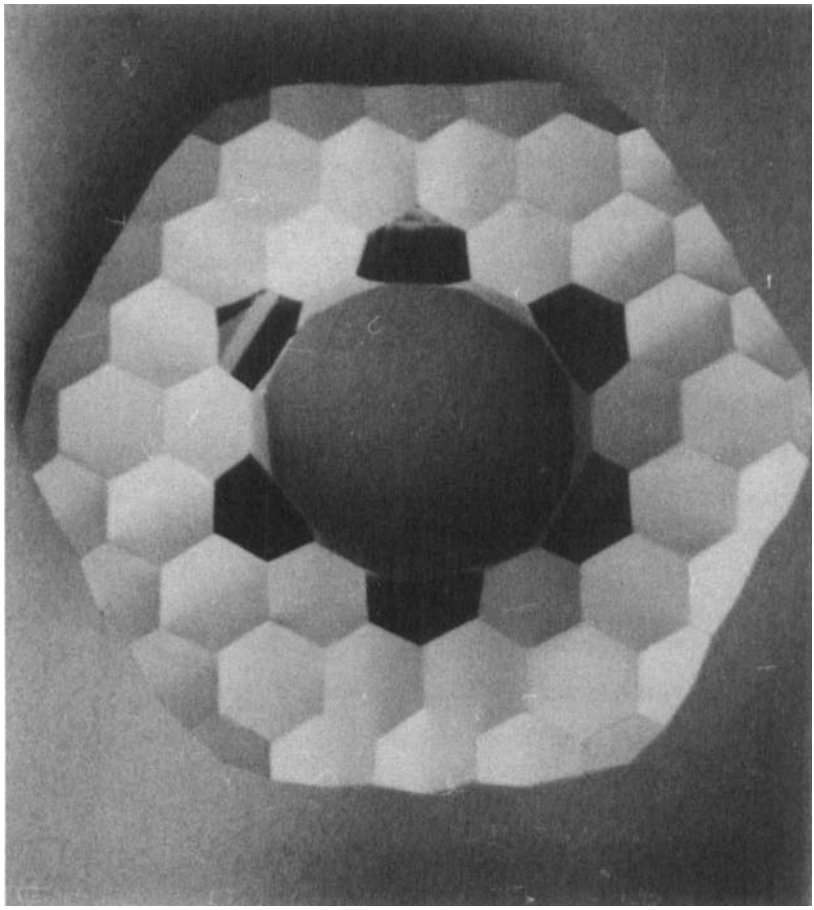

Fig. 5. The model of cluster (IY).

data on the ionisation potentials and electron affinity of C_{60} fullerene[2] (α = -3.5 eV, β = -6,6 eV) we get that the ionization potential of cluster (II) should be close to graphite ionization potential (5.5 eV) and equal to 5.9 eV.

Clusters (I), (III) and (IV) as opposed to cluster (II) contain π-electron number divisible by 4. Probably this is the reason of the fact that cluster (I) and (IV) electronic shells are not closed. Cluster (III) has a pseudo-closed electronic shell. Results of our

calculations prove that π-electron system of such 4n-carbon clusters can hardly be sufficiently kinetic stable. That is why searching for torus-like clusters preference should be given to toroids consisting of (4n + 2) carbon atoms.

After completing present paper, we became acquainted with a similar study of torus-like objects[13,14]. Note that the carbon cages C_{540} and C_{576} considered in [13] are related to 4n π-electron clusters. According to our assumptions, their gaps are also nearly zero.

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