Simulation of geometrical and electronic structure of quasi-two-dimensional layer consisting of fullerenes D_{6h}-C_{36}

Elena G. Gal'pern,* Ivan V. Stankevich,* Anatolii L. Chistyakov,* and Leonid A. Chernozatonskii†

*Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow, 117813, Russia
†Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygin St., Moscow, 117971, Russia

This article describes a computer simulation of the geometrical and electronic structure of a quasi-two-dimensional carbon layer with a trigonal lattice consisting of fullerenes C_{36} (1) with topological symmetry D_{6h}. Every polyhedral cluster 1 of this polymeric layer (2) is surrounded by six similar fullerenes and connected with every such a fullerene by two covalent bonds. Atomic coordinates of the repeating unit are estimated on the basis of MNDO/PM3 calculations of hydrocarbon molecule (D_{6h})-$C_{132}H_{48}$ (3). The carbon skeleton of 3 coincides with a sufficiently large fragment of the polymeric layer 2. The electronic spectrum of the quasi-two-dimensional layer 2 is calculated by the crystalline orbital method in the EHT approximation. The band gap in the electronic spectrum of 2 was found to be equal to 1.5 eV. The geometric and electronic structure of some oligomers of cluster C_{36}, quasi-linear macromolecule $[C_{36}]_n$, and "hypergraphite" layer is also discussed. © 2001 by Elsevier Science Inc.

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In the last few years small fullerenes, and especially clusters C_{36} (1), have attracted the attention of researchers. Interest in this class of compounds has been connected principally with an article[1] that discussed the arc method production of polycrys-

talline carbon patterns consisting of fullerenes C_{36}. Analysis of the spectrum of ^{13}C-NMR and electron diffraction show that this substance seemingly consists of clusters of C_{36} with topological symmetry D_{6h} (Figure 1).

Note that the stability of fullerene C_{36} and its higher barrel-shaped (b) homologs (D_{6h})-(b)-C_{36+12n} ($n = 1, 2, \ldots$) and also superconducting properties of their crystals doped by alkali atoms were discussed as early as 1992 in our article.[2]

Properties of clusters C_{36}, as well as some oligomeric and polymeric molecules on the base of C_{36}, have been studied recently in theoretical papers.[3–9] For instance, it has been shown[5] that cluster (D_{2d})-C_{36} is the most stable of all isomers of fullerene C_{36}. In addition, cluster (D_{6h})-C_{36} is transformed into a more stable but less symmetrical one of C_{6v} symmetry. That is a result of energy degeneration of the ground state of cluster (D_{6h})-C_{36}. It has been shown[2] in the Hückel approach that (D_{6h})-(b)-C_{36}, (D_{6h})-(b)-C_{60}, (D_{6h})-(b)-C_{72}, and other fullerenes with a similar barrel structure have partly occupied binding orbitals. Each such cluster has a deficit of two electrons for formation of a closed electron shell (in the Hückel sense). Therefore, clusters (D_{6h})-(b)-C_{36+12n} ($n = 1, 2, \ldots$) must be inclined to form dianions. MNDO calculations show[2] that dianion (D_{6h})-C_{36}^{2-} has a closed electron shell. Negative charge in the dianion is localized principally on atoms (C^α atoms) disposed in the α positions relative to polar hexagons (see Schlögel diagram in Figure 2). Therefore, such C^α-atoms of neutral cluster must be the most reactive ones. Thus, favorable conditions are produced for formation of dimers of cluster C_{36} or its oligomers with covalent bonds between C^α-atoms of conforming monomers. At the same time, covalent binding of negatively charged clusters C_{36} must be considerably less probable. This conclusion corresponds to that of Zettl et al.[7] that

Corresponding author: I.V. Stankevich, Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow, 117813, Russia. Tel.: +7(095) 135-7998; fax: +7(095) 135-5085.
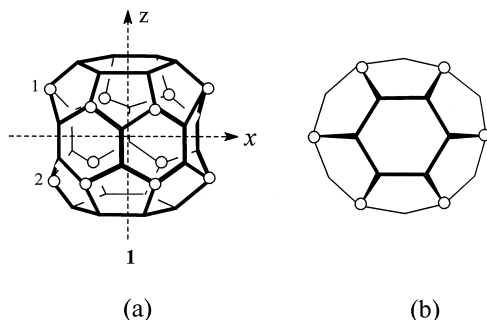
E-mail address: stan@ineos.ac.ru

*Figure 1. (a) Fullerene C_{36} (**1**); (b) top view of C_{36}; C^{α}-atoms placed in the α-positions relative to polar hexagons are denoted by circles; axis z coincides with axis symmetry C_6.*

negatively charged clusters (D_{6h})-C_{36} have less tendency to form dimers than neutral ones.

Oligomeric and polymeric structures of cluster (D_{6h})-C_{36} are discussed elsewhere[3,4,6]. A quasi-two-dimensional layer ("supergraphite") (Figure 3), consisting of superbenzene moieties is studied in an article by Fowler et al.[6] Superbenzene (Figure 4) consists of a six-membered macrocycle in every vertex where cluster C_{36} is disposed and adjacent clusters are bound by two covalent bonds. Note that the supergraphite layer considered by Fowler et al.[6] is a sufficiently porous one and contains large cavities. We show that in every such cavity there can be yet a cluster C_{36} connected with each of six nearest neighbors by two covalent bonds. As a result, a trigonal lattice **2** is generated (Figure 5). Only one cluster C_{36} occurs in every node of this lattice. Such a close-packed quasi-two-dimensional layer **2** is possible and its conducting properties are of large interest.

Simulation of geometrical and electronic structure of this quasi-two-dimensional layer **2** is the principal aim of this article.

CALCULATION PROCEDURE

Geometrical structure of a repeating unit of the quasi-two-dimensional macromolecule **2** and its nearest environment are found in the MNDO/PM3 calculation of hydrocarbon molecule (D_{6h})-$C_{132}H_{48}$ (**3**) (see Figure 5b) using the GAMESS program package [10] on a DEC 3000 Alpha AXP 400X workstation. Electron energy spectra of periodical structures have been
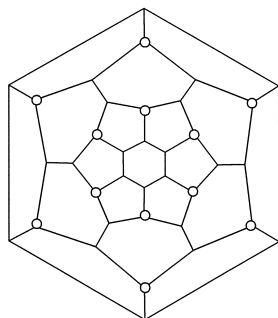

Figure 2. Schlögel diagram of fullerene C_{36} with topological symmetry D_{6h}.
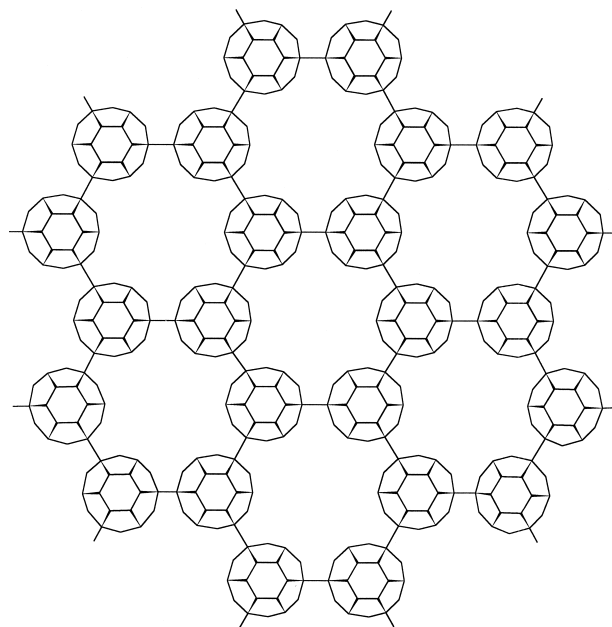

*Figure 3. Top view of "supergraphite" layer **2** of clusters C_{36}; axis z is perpendicular to the figure plan.*

obtained in the EHT approximation[11] by the crystal orbital method using the LATTIC program.[12]

RESULTS AND DISCUSSION

Fullerene **1** with topological symmetry D_{6h} is represented in Figure 1 where its side and top views are shown. Hybridization of every atom of (D_{6h})-C_{36} is the sp^2. Calculations of singlet and triplet states of C_{36} without symmetry restrictions show that local minima exist on conforming potential energy surfaces.

The ground state of fullerene **1** is a triplet and its group symmetry is C_{2v} (the axis C_2 is axis x, see Figure 1). Symmetry of the calculated singlet state is C_6 only (the axis C_6 coincides with the axis z). Energy of this state is larger than that of the triplet state on $\sim$25 kcal/mol^{-1}. Comparison of geometrical
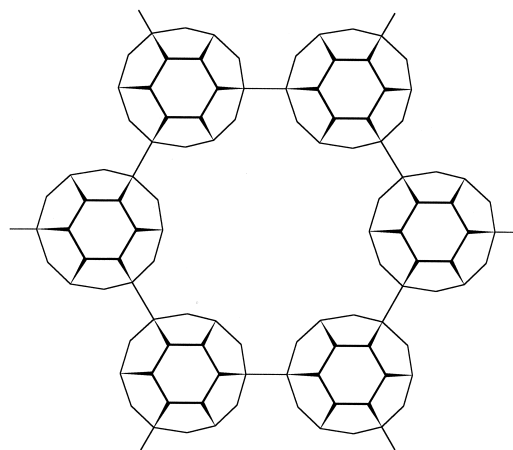

Figure 4. Top view of "superbenzene"; axis z is perpendicular to the figure plan.

labeled with numbers 1 and 2). Besides deviation from sp^2, the hybridization of these atoms is increased: the sum deviation of valence angles from 360° is equal to 18°. Therefore, these atoms are most adapted to bind with two similar atoms of other monomers with formation of dimers (D_{2h})-$(C_{36})_2$ (**4**) in which monomers are bound by two sp^3—sp^3 covalent bonds (Figure 6). Oligomers of a different configuration can form clusters of C_{36}: for example, linear (**5**, D_{2h}) and triangular (**6**, D_{3h}) trimers containing 108 atoms (Figure 6). MNDO/PM3 calculations with symmetry retention of dimer (**4**) and these two trimers show local minima to exist on the conforming potential energy surfaces. Oligomerization energy (on one monomer) is determined as the difference between the sum of the ground state energies of noninteracting monomers and the ground state energy of the conforming oligomer divided by number of monomers. Oligomerization energy values for clusters **4**–**6** are 2.3 (**4**), 3.8 (**5**), and 3.0 (**6**) eV, respectively.

It follows from the data that it is sufficiently advantageous at the energy formation of dimer **4**, linear and trigonal trimers **5** and **6** from monomers C_{36}. Note that average values of energy bond C—C between monomers in oligomers **3**–**5** are equal to 2.3, 2.9, and 1.5 eV, respectively. Values of the vertical ion-
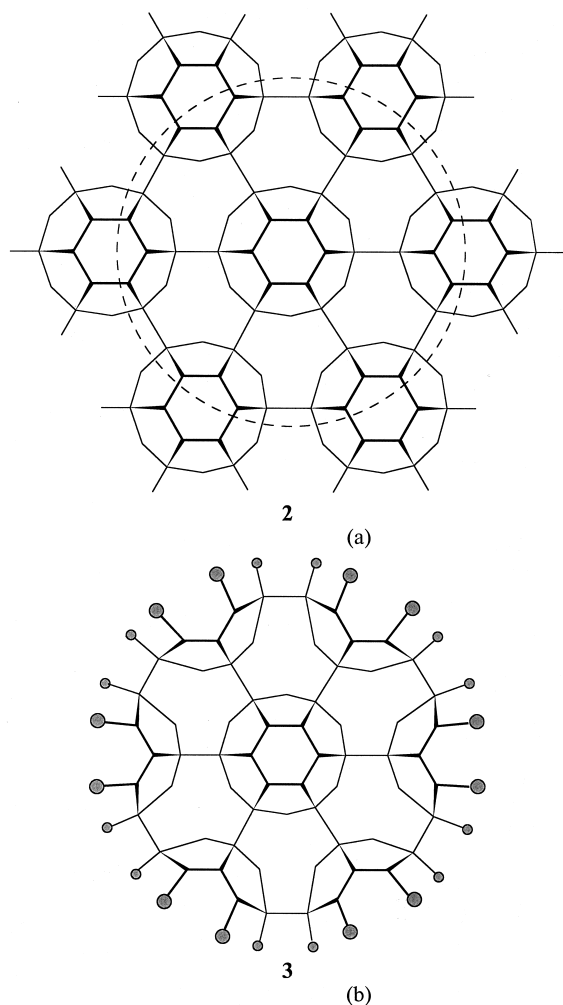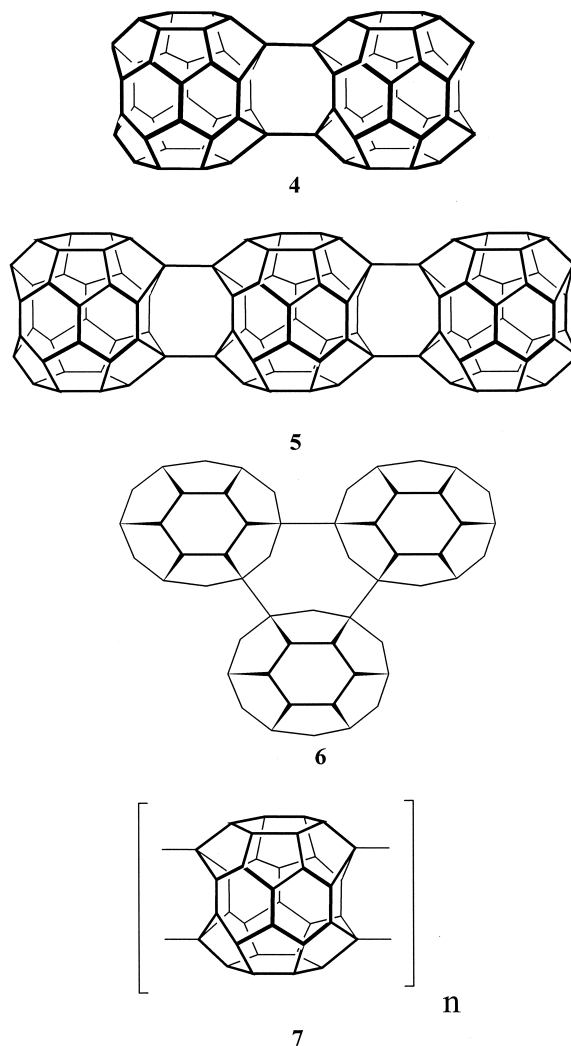

2

(a)

3

(b)

*Figure 5. (a) Top view of quasi-two-dimensional layer (**2**); dotted line is the cylinder projection on the plane (x, y); inside, the cylinder contains 132 atoms of central cluster C_{36} and its six neighbors; (b) above view of hydrocarbon $C_{132}H_{48}$ (**3**) obtained under substitution of bonds C—C ≪broken≫ by cylinder on C—H bonds; atoms H are denoted by cyrcles.*

parameters of singlet and triplet states of C_{36} shows bond lengths between atoms of polar faces coincide with precison of 0.01–0.02 Å.

Bonds of C^α atoms with hexagon atoms arranged on the side surface of C_{36} differ most strongly. Lengths of these bonds in the singlet state of (C_6)-C_{36} are equal to 1.472 Å, whereas other bonds become shorter and change from 1.395 to 1.446 Å.

In the singlet state of this cluster the distance between six-membered polar cycles is equal to 5.2 Å. The shape of every hexagon on the side surface of C_{36} is a boot. C^α-atoms occur at the distance of 2.31 Å from the symmetry axis. Sum deviations of valence angles at C^α-atoms from 360° characterizing its deviation from sp^2 hybridization is equal to 10°. Notice also that the equivalence of C^α-atoms in the ground triplet state with C_{2v} symmetry is disturbed. The spin density in the triplet state principally localizes on two C^α-atoms arranged in plane σ_v with one side cluster C_{36} (see Figure 1, atoms

4

5

6

7

*Figure 6. Oligomers **4**–**6** and linear chain **7** based on C_{36}.*

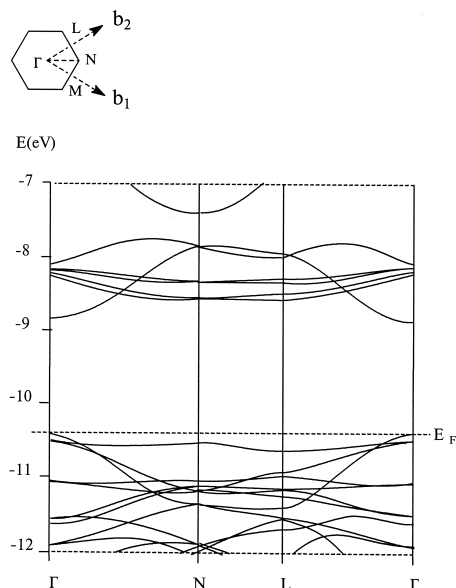Fig. 7. *Electron spectrum of close-packed polymer layer* **2**; E_F – *the Fermi level.*

Figure 8. *Electron spectrum of linear macromolecule* **7**; E_F – *the Fermi level.*

ization potentials of these clusters are equal to 8.9 (**4**), 8.9 (**5**), and 9.13 (**6**) eV.

Triangular trimer **6** can be considered as a fragment of the polymeric layer **2** with a trigonal lattice. Figure 5 shows a top view of this layer fragment. Cluster C_{36} can be chosen as a repeating unit of layer **2**. Atomic coordinates of this repeating unit and translation vectors of **2** are estimated from MNDO/PM3 calculation results of hydrocarbon molecule (D_{6h})-$C_{132}H_{48}$ (**3**). Figure 5 shows a top view of this moiety. Molecule **3** consists of central cluster (D_{6h})-C_{36} and six bowl-shaped hydrocarbon biradicals $C_{16}H_8$ connected with central cluster C_{36} and adjacent similar moieties by pair chemical bonds. A dotted line in Figure 5 shows projection of a cylinder perpendicular to the layer **2** cylinder. The carbon skeleton of **3** coincides with a fragment of the carbon skeleton of **2**, atoms of which are disposed inside this cylinder. It follows from the calculations that the electron shell of **3** is closed. Energies of the HOMO and LUMO are distinguished by 2.56 eV. The vertical ionization potential is equal to 5.5 eV. A detailed analysis of the molecular structure considered shows that geometrical parameters of central cluster C_{36} in molecules **3** are a sufficiently good approximation for simulation of geometrical structure of the quasi-two-dimensional layer **2**. Note that bond C—C length between two adjacent clusters C_{36} depends weakly on the system under consideration. These values for moieties **4**–**6** are equal to 1.545 (**4**), 1.547 (**5**), 1.553 (**6**), and 1.572 (**3**) Å, and differ a bit from the average length of a simple bond C—C. Minor increasing of C—C bond length for molecule **3** indicates an occurrence of extra steric strain in this moiety. Cluster C_{36} in **3** becomes lower and wider. Height and width (in brackets) of insulated cluster C_{36} is equal to 5.21 (4.62) Å; values for molecule **3** are close to 5.00 (5.08) Å. The translation vector lengths of layer **2** found in the calculation results of molecule **3** are equal to ≈6.65 Å. This value is close to the experimental parameter of an elementary unit (6.7 Å) of polycrystalline patterns of C_{36} produced by Piskoti et al.[1] Figure 7 shows the structure of electron spectrum zones of this
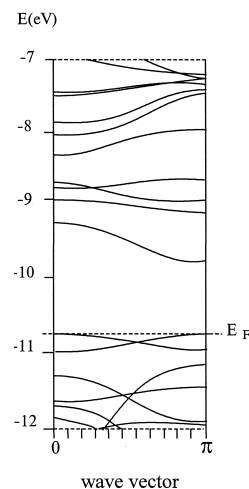
macromolecule **2** calculated at atomic coordinates found by geometry optimization of the molecule **3**. It should follow from Figure 7 that the polymeric layer **2** must have semiconducting properties because the HOMO–LUMO gap in its electron spectrum is equal to ~1.5 eV. Similar calculations of the band gap for the "supergraphite" layer (Figure 3) show that in this case the HOMO–LUMO gap is equal to 1.75 eV.

Analysis of band gap dependence from the dimensions of the lattice has been also carried out on an example of a linear chain **7** (Figure 6). Atomic coordinates of the repeating unit and translation vector are found from an optimized structure of trimer **5**. Figure 8 shows electron spectrum zones of **7**. It is evident from this figure that the gap in the electron spectrum of **7** is equal to 1 eV. Thus, the gap in a quasi-one-dimensional system **7** is smaller than that in a close-packed quasi-two-dimensional layer **2**. A similar result at the DFTB level has been obtained by Fowler et al.[6] for linear and supergraphite systems based on C_{36}. The band gaps in these cases are equal to 1.28 and 2.09 eV, respectively. The increasing gap of a quasi-two-dimensional layers relative to that of a quasi-one-dimensional macromolecule can be a result of the extent of decrease of the conjugated systems of these two-dimensional lattices in comparison with a one-dimensional one. Thus, conjugated system **2** consists only of very weakly interacting insulated hexagons arranged perpendicular to axis *z*, while side atoms of clusters C_{36} connecting similar hexagons in **7** are also contained in its conjugated system.

CONCLUSION

In the calculations described above, we have shown stability of close-packed layer **2** consisting of covalently bound clusters C_{36} and found that this carbon modification, as well as "hypergraphite,"[6] must be semiconductor. Results of C_{36}-based linear chain and "hypergraphite" computer simulation obtained in the present paper by simple semi-empirical methods of quantum chemistry correspond to data of the DFTB model used by Fowler at al.[6]

ACKNOWLEDGMENTS

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