FULLERENES
AND ATOMIC CLUSTERS

Correlation of the Chemical Properties of Carbon Nanotubes with Their Atomic and Electronic Structures

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Abstract—The nature of chemical bonding in carbon nanoclusters is investigated by the PM3 semiempirical quantum-chemical method. The influence of the atomic structure on the electronic characteristics and chemical properties of nanoclusters is analyzed. A σ–π model is proposed for the chemical bonding in nanotubes. It is shown that, in the framework of the proposed model, nanotubes are objects characterized by a small contribution of π states to the valence band top. © *2004 MAIK "Nauka/Interperiodica".*

1. CHOICE OF THE OBJECTS FOR INVESTIGATION

The specific feature of elemental carbon is its ability to form a great variety of complex spatial structures consisting of polygons. Nanotubes were theoretically predicted by Kornilov [1, 2] in 1977 and Chernozatonskii [3] in 1991 and were found experimentally by Ijima [4] in 1991. To date, nanotubes have been used as materials for designing macromolecular structures up to hundreds of nanometers in size. The discovery of nanotubes has attracted considerable attention due to the possibility of preparing materials with unusual physicochemical properties.

In this work, we investigated the nature of chemical bonding in carbon nanoclusters and analyzed how their atomic structure affects the electronic characteristics. For model calculations, we chose two structures with the same set of atoms located in a circle of a carbon cylinder. These were zigzag (10, 0) and armchair (5, 5) nanotubes, which differ in terms of the mutual arrangement of hexagons (with respect to the longitudinal axis of the tube) and radii. The choice of the tube sizes was limited by the computational power. In particular, the number of atoms in nanotubes was varied from 150 to 250 and the tube length was varied from 15 to 25 nm. Dangling chemical bonds at the ends of carbon nanoclusters were terminated by hydrogen.

Calculations of the nanotubes were performed by the PM3 semiempirical method [5] with the GAMESS program package [6]. Semiempirical methods offer an adequate description of both the atomic structure (bond lengths, bond angles) and electronic structure (photoelectron spectra), which has been confirmed in a num-

ber of works (see, for example, [7, 8]). Moreover, the PM3 method makes it possible to calculate the electronic and atomic structures of sufficiently large-sized clusters.

2. CALCULATION OF THE ELECTRON DENSITIES OF STATES

The electronic structure was analyzed in terms of densities of states. We constructed an energy spectrum of a molecule in which each molecular orbital was represented by one line. The intensities of all lines were taken equal to unity. Then, each line was replaced by a Gaussian distribution whose half-width at half-maximum was equal to 0.1 eV. The intensities of all the distributions at each energy were summarized.

When constructing the partial densities of states of atomic orbitals x, the intensity of each line corresponding to the molecular orbital y was taken equal to the sum of the squares of the coefficients of the atomic orbitals x in the LCAO MO expansion of the orbital y. Then, the partial density of states was constructed by the algorithm used to construct the total density of states.

In standard quantum-chemical programs, the wave functions of the P orbitals for each atom are oriented in a global coordinate system. In order to interpret the partial densities of states for molecules with spherical and cylindrical symmetry, the basis set calculated for each carbon atom is sometimes transformed from the global coordinate system into a local coordinate system through the Euler transformation. In the case of nanotubes, this is a cylindrical transformation with respect
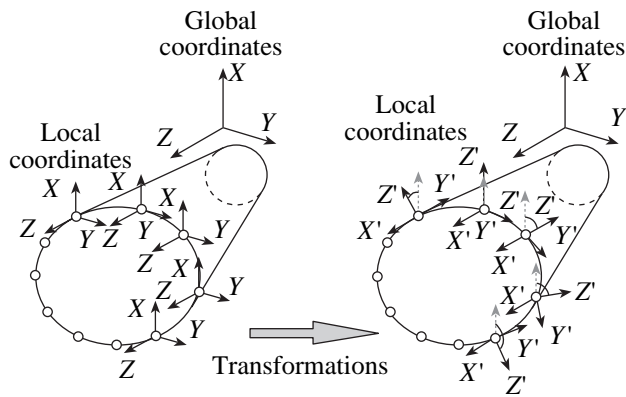
Fig. 1. Transformation of the *P* wave functions of carbon from a global coordinate system into a local coordinate system for nanotubes.
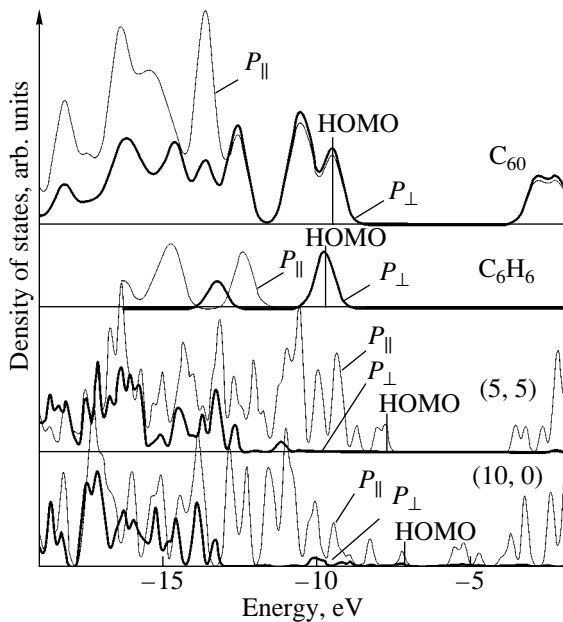

Fig. 2. Partial densities of $P_\parallel$ and $P_\perp$ states for carbon nanostructures.

to the longitudinal axis of the tube, when one of the *P* orbitals of a carbon atom is oriented normally to the tube surface (Fig. 1). The transformation of the basis set results in a set of orbitals oriented normally ($P_\perp$) and tangentially ($P_\parallel$) to the tube surface.

3. RESULTS OF CALCULATIONS OF NANOCLUSTERS

The nature of chemical bonding was investigated by comparing the electron densities of states. The densities of states were compared for the *P* orbitals directed both tangentially to the molecular plane ($P_\parallel$, σ bonding) and normally to the tube surface ($P_\perp$, π bonding) (Fig. 2).

When investigating nanotubes, it is of interest to compare the electronic structures of fullerenes (with a spherical structure) and benzene (with a planar structure) (Fig. 2). It can be seen from Fig. 2 that the upper levels in the valence band of benzene are characterized only by the π ($P_\perp$) bonding, whereas the $P_\parallel$ and $P_\perp$ states are mixed (with approximately equal contributions) for C_{60} fullerene [9]. The benzene molecule has the shape of a regular hexagon, the σ ($P_\parallel$) and π (P_z or $P_\perp$) bonds differ in energy, and the upper orbitals consist only of the P_z ($P_\perp$) orbitals. The C_{60} fullerene molecule is icosahedral in shape, and undistorted hexagons form faces of the structure. The curvature of the surface leads to mixing of the P_z ($P_\perp$), P_x ($P_\parallel$), and P_y ($P_\parallel$) orbitals, and the upper valence levels are composed of the $P_\perp$ and $P_\parallel$ states.

Figure 2 shows the partial densities of $P_\parallel$ and $P_\perp$ states for the calculated carbon nanotubes. As can be seen from Fig. 2, the electron wave functions that are aligned normally and tangentially to the surface of the structure and, correspondingly, determine the σ ($P_\parallel$) and π ($P_\perp$) bonding appear to be mixed as a result of the surface curvature of the carbon nanotube. The nature of chemical bonding in nanotubes is governed by the ratio of the contributions from these wave functions to the molecular orbitals. The upper filled levels in the valence band of nanotubes involve, for the most part, the $P_\parallel$ states and a small number of the $P_\perp$ states. The nanotubes have a cylindrical structure. Hence, from general considerations, the ratio of the contributions from the $P_\perp$ and $P_\parallel$ wave functions to the valence band top should be intermediate between the corresponding ratios for benzene and fullerenes. Let us discuss why this is not the case.

First, we analyze the nature of chemical bonding in the (5, 5) and (10, 0) nanotubes. A comparison of the partial densities of states for the (5, 5) and (10, 0) tubes shows that the contribution from the $P_\perp$ bonding is somewhat larger in the electronic structure of the (10, 0) tube. This can be explained by the larger diameter and, hence, by the smaller surface curvature of the tube, which leads to a larger overlap between the $P_\perp$ orbitals and an increase in the contribution of the $P_\perp$ orbitals to the upper occupied molecular orbital (the valence band top). However, the aforesaid does not explain the small contribution of the $P_\perp$ bonding to the valence band top, even though these nanotubes are comparable in diameter to C_{60} fullerene [$d(n, n) < d(2n, 0)$, $d(5, 5) = 6.78$ Å, $d(10, 0) = 7.83$ Å, $d(C_{60}) = 7.09$ Å].

4. DISCUSSION

As was noted above, compared to fullerenes, nanotubes should possess a sufficiently high density of $P_\perp$ states at the valence band top. Carbon nanotubes are intermediate in structure between planar benzene (and graphite) and ideally spherical fullerene C_{60} (symmetry

I_h). The large scatter in the diameters of nanotubes leads to mixing of the P_z ($P_\perp$), P_x ($P_\parallel$), and P_y ($P_\parallel$) orbitals in the valence band, as is the case with fullerenes. However, the contribution from the P_z ($P_\perp$) orbitals to the top of the valence band is smaller in nanotubes.

In order to answer the question as to why the electronic structure of nanotubes possesses such specific properties, it is necessary to change over from considering their geometric structure (tube radius, tube length) to a detailed analysis of the atomic structure of hexagons forming a carbon skeleton of the tube.

The bond angles in hexagons of all the structures remain constant throughout the tube and are approximately equal to 120° (typical angle for the sp^2 hybridization), as is the case in benzene, graphite, and fullerene hexagons. The scatter of internuclear distances in nanotubes also slightly differs from the scatter characteristic of fullerene molecules and, hence, like the bond angle, does not affect the redistribution of the $P_\parallel$ and $P_\perp$ bonding.

An analysis of the torsion (dihedral) angles (Fig. 3) describing polygon distortions (deviations from the planarity) revealed an interesting regularity. In all nanotubes, the structure of all polygons is strongly distorted.

In the structure of the (10, 0) tube, the torsion angle in hexagons (angle between the planes formed by *1–2–3–4* and *4–5–6–1* carbon atoms; see Fig. 3a) is approximately equal to 18°. The hexagon plane is folded so that the fold line is parallel to the tube axis. In the structure of the (5, 5) tube, the torsion angle in the hexagon is approximately equal to 24°. The hexagon plane is folded, and the fold line in the hexagon is perpendicular to the tube axis (Fig. 3b).

The torsion angle in the (5, 5) structure is, on the average, 6° larger than that in the (10, 0) structure. The hexagon structure in the former nanotubes is formed by two well-defined planes. In the (10, 0) nanotubes, two less pronounced planes can also be distinguished in the distorted structure of hexagons. It can be seen from Fig. 2 that the density of $P_\perp$ states at the valence band top is higher for the (10, 0) nanotube characterized by a smaller distortion of the hexagon structure, and vice versa.

Therefore, the smaller the distortion of hexagons in the structure of the carbon nanotube, the larger the overlap of the $P_\perp$ orbitals, which, in turn, results in an increase in the density of $P_\perp$ states at the valence band top. As a consequence, strong distortions of carbon hexagons lead to a change in the character and energy of overlap between the $P_\perp$ orbitals and to an increase in the contribution of the σ bonding.

Owing to specific features in the geometry, the hexagons forming the surface of carbon nanostructures are distorted in the vast majority of carbon nanoobjects. These spatial distortions are responsible for the substantial differences in the electronic structure.
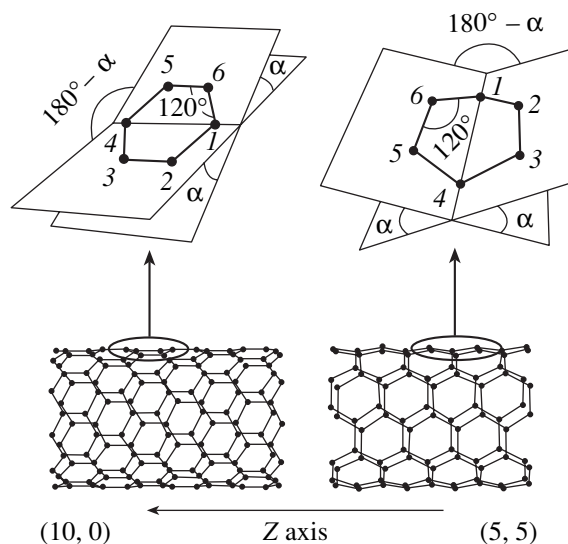

Fig. 3. Torsion angles of (a) (10, 0) and (b) (5, 5) carbon nanotubes.

In the case of planar molecules (benzene, graphite), the overlap between the P_z orbitals leads to the formation of typical π bonds. Since the fullerene molecule is spherical in shape, the overlap of the P_z orbitals above the molecular plane is not equivalent to that below the molecular plane. This gives rise to mixed states formed by σ and π bonds. The distortion of nanotube hexagons results in a shift of the overlap between the P_z orbitals toward the low-energy range, and, hence, the contribution of the P_z orbitals to the valence band top for nanotubes is small. The above analysis of the electronic structure permits us to elucidate particular chemical properties of carbon nanoclusters.

Fullerene molecules possess an electron affinity and act as weak oxidants in chemical reactions. This can be observed, for example, in the hydrogenation of C_{60} fullerene with the formation of $C_{60}H_{36}$ as the reaction product [10]. At room temperature, C_{60} fullerene oxidizes only under irradiation with photons, which is explained by the formation of negative O_2^- ions with a high reactivity [10]. The composition of the products of fullerene fluorination substantially depends on the reaction conditions. The reaction of C_{60} with NaF at $T = $ 500–550 K predominantly leads to the formation of $C_{60}F_{46}$ (with addition of 10–15% $C_{60}F_{48}$). Chlorination of C_{60}, as a rule, results in the formation of compounds containing either 12 or 24 chlorine atoms. Moreover, fullerene participates in addition reactions with the formation of products involving hydrogen radicals, phosphorus, halogens, metals and their oxides, benzene rings and their derivatives, NO_2, alkyl radicals, etc. [10].

As a rule, approximately 5–8% of carbon atoms in nanotubes undergo chemical transformation under soft conditions depending on the type of carbon structures

and reactants. Usually, these atoms belong to defects in the nanostructure. In this case, the terminal atoms have a higher reactivity as compared to atoms located on the nanotube surface. Under sufficiently severe conditions (strong acids, high temperatures, plasma activation, etc.), more than 50% of carbon atoms undergo chemical transformation. This leads to a change in the properties of nanotubes, in particular, to a decrease in the stability [11–16].

Owing to formally identical sp^2 hybridization, the same type of carbon–carbon bonds, and the predominance of hexagons in all structures, fullerenes and nanotubes should resemble graphite in terms of their chemical properties. Actually, nanotubes (compared to fullerenes) are similar in terms of their chemical properties to graphite, because they are rather inactive in reactions.

The chemical properties of fullerenes can be explained by the difference in the overlap of the $P_\perp$ orbitals above and below the molecular plane due to the sphericity of the molecule. The overlap density above the fullerene surface is lower. As a result, the corresponding orbitals are more susceptible to attacks by electrophilic agents. For this reason, fullerene more easily enters into chemical reactions as compared to graphite, in which the overlap densities of the $P_\perp$ orbitals above and below the plane are identical to each other. For benzene, the configuration of the $P_\perp$ orbitals is the same as for graphite. As a consequence, reactions of substitution for hydrogen rather than reactions of electrophilic addition to the π cloud are characteristic of benzene.

All the aforementioned features of fullerene molecules allow us to draw the conclusion that nanotubes should also readily enter into addition reactions. Since the geometry of nanotubes is similar to that of fullerenes, the overlap of the $P_\perp$ orbitals above and below the tube surface should also be similar to the overlap in fullerene. However, this is not the case, because all hexagons in nanotubes are strongly distorted. As a result, the contribution of the π states to the valence band top is small, since these states are shifted to the low-energy range. Therefore, the reactivity of nanotubes is considerably lower than that of fullerenes.

5. CONCLUSIONS

Thus, the electronic structure of carbon nanotubes was investigated in the framework of the σ–π model. It was shown that carbon nanotubes are objects characterized by a small contribution of the π states to the valence band top. The surface curvature of carbon nanostructures leads to mixing of the atomic orbitals aligned tangentially and normally to the surface. The ratio of the contributions from these wave functions determines the nature of chemical bonding in the nanostructures. Owing to specific features in the geometry, all hexagons forming the tube wall are strongly distorted in all carbon nanotubes. These spatial distortions of hexagons are responsible for the substantial differ-

ences in the electronic structure. The distortion affects the character and energy of overlap between the P_z orbitals, which leads to an increase in the contribution of σ bonding and, correspondingly, to a decrease in the contribution of π bonding to the upper occupied orbitals. Therefore, the smaller the distortion of hexagons in the structure of carbon nanotubes, the larger the overlap of the $P_\perp$ orbitals.

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