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Effect of local strain on the reactivity of carbon nanotubes

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The heats of addition of H atom and Me$^\bullet$ radical to carbon atoms of a capped (10,10)-nanotube were calculated by the molecular dynamics (MD) method with Brenner´s potential. According to calculations, the reaction heats linearly depend on the pyramidalization angle, which is a quantitative measure of the local curvature and strain in the planar carbon sheet in the vicinity of the reaction center. Depending on the pyramidalization angle (0—20°), the change in the reaction energy can reach 1 eV. Comparison of the results obtained for a model reaction $CH_3^\bullet + H^\bullet \rightarrow CH_4$ using the *ab initio* approach and MD simulations with Brenner´s potential shows that this potential can be used in studies of the effect of pyramidalization of the carbon center on its reactivity.

Key words: nanotubes, functionalization, pyramidalization angle, molecular dynamics.

Carbon nanotubes (CNT) possess some interesting properties. Of particular interest are mechanical and electrical properties of CNT.[1] An infinite CNT can be represented in the form of a strip rolled into a cylinder cut from a graphite sheet. The structure of such a CNT is described by two integer indices (n,m) characterizing helical arrangement of the atoms with respect to the nanotube axis. Depending on the $n - m$ difference, the electronic spectra of CNT can be of metallic or semiconductor type.[2—5] For instance, if $n - m = 3q$ (q is an integer), the CNT are metals, otherwise they are semiconductors.[6]

Recently, emphasis has been placed on the studies of electrophysical properties of CNT. This is due to the obtaining of new experimental and theoretical results[7—16] that allowed the researchers to suggest that CNT-based electronic devices will not be nanoscale analogs of the known macroscopic devices because of their quasi-one-dimensional electronic structure leading to new physical phenomena. Research in the field of fundamentals and possible applications of the electrophysical properties of CNT involves studies of, *e.g.*, heterojunctions,[7,8] diodes,[9] quantum dots,[10—12] field effect transistors,[13—15] and single-electron conductors.[16]

Fabrication of CNT with practically valuable properties requires modification of their electronic structure. Electronic properties of CNT are very sensitive to the influence of external factors. A promising way of targeted changes in the electronic structure of CNT is their chemical modification (in particular, functionalization). Mention may be made of some interesting studies in this field, namely, the attachment of H atoms to strained (mechanically deformed) sections of CNT,[17] consideration of the problem of embedding the C_2 dimers into strained segments of CNT to form quantum dots,[18] and modeling of irradiation of the CNT surface with energetic Me$^\bullet$ radicals.[19] However, these studies revealed no quantitative relationships between the reactivity and any properties of carbon sheet.

Studies of model reactions of the simplest hydrocarbons revealed a correlation between the deviation of a given (reacting) sp^2-hybridized C atom from the plane passing through three adjacent carbon atoms and the reactivity of this atom.[20] The pyramidalization angle (PA) was introduced as a measure of the deviation from this plane.[20] For a tricoordinated carbon atom, the PA is defined as follows: from the nucleus of a given atom, a vector is drawn so that it makes equal angles $\theta_{\sigma\pi}$ with the directions of the bonds with the adjacent C atoms. Then, the PA, θ_P, is calculated as the difference $\theta_P = \theta_{\sigma\pi} - 90°$. The PA is 0° for sp^2-hybridized C atom and is ~19° for sp^3-hybridized C atom. The PA value is used[21] as a measure of the local Gaussian curvature, k, of the surface on which the CNT atoms are arranged. The θ_P and k values are related by an approximate formula $k = 2\sin\theta_P/a$, where a is the average distance to adjacent atoms.

The idea of PA was previously used for assessing the contributions of the atom—atom interactions to the strain energy of σ-skeletons of carbon cages and the extent of

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reduction of local contributions to the π-electron energy (relative to the planar system).[22] These values are quadratic functions of the PA (θ_P): for instance, the σ-strain energy is proportional to $\sim 0.5k\theta_P^2$, where k is the force constant. Analogous quadratic dependences on the PA were also found[23] for the heats of formation of fullerenes obtained from MNDO calculations.

This work concerns modeling of chemical reactions in strained molecules. The concept of PA [20] was used for the description of addition reaction of $\mathrm{Me}^{\bullet}$ radical and H atom to the carbon atoms of a CNT.

Calculation Procedure

The addition reaction of H atoms and $\mathrm{Me}^{\bullet}$ radical to carbon atoms of a (10,10)-CNT capped at one end was simulated by the molecular dynamics[24] (MD) method with Brenner´s potential.[25] The shape of the carbon cluster is described by a fragment of a capped cylindrical surface comprising a total of 354 atoms. From the complete list of topologically different isomers with isolated pentagons (a total of 9342 structures[26,27] for the (10,10)-CNT) we chose an unsymmetrical cap containing 100 atoms characterized by a wide range of PA values. As the initial state we used a CNT with preliminarily fully optimized geometry.[24] Optimization was carried out with inclusion of "friction forces" ($F_{mp}{}^{i} = -\gamma v_i$, where $\gamma = 0.99$ and v_i is the velocity of ith atom), which were added to the analytically calculated atom—atom interaction forces.

The Brenner potential can be written as the sum of the bond energies:

$$E = \sum_{i} \sum_{j(>i)} [V_{\mathrm{R}}(r_{ij}) - \bar{B}_{ij} V_{\mathrm{A}}(r_{ij})], \qquad (1)$$

where $V_{\mathrm{R}}(r_{ij})$ and $V_{\mathrm{A}}(r_{ij})$ are the pair exponential repulsive and attractive terms (of the type of the generalized Morse potential) for adjacent atoms i and j separated by a distance r_{ij}. The $\bar{B}_{ij}$ coefficient depends on the atoms in the second and third coordination spheres of the atoms i and j and on the type of the i—j bond and is defined as follows

$$\bar{B}_{ij} = (B_{ij} + B_{ji})/2 + F_{ij}(N_i^{\mathrm{t}}, N_j^{\mathrm{t}}, N_{ij}^{\mathrm{conj}}). \qquad (2)$$

In this expression

$$B_{ij} = [1 + \sum_{k(\neq i,j)} G_i(\theta_{ijk}) f_{ik}(r_{ik}) \exp\{\alpha_{ijk}[(r_{ij} - R_{ij}^{\mathrm{e}}) - (r_{ik} - R_{ik}^{\mathrm{e}})]\} + H_{ij}(N_i^{\mathrm{H}}, N_i^{\mathrm{C}})]^{-\delta_i}, \qquad (3)$$

where $G_i(\theta_{ijk})$ is a function of the angle between the j—i and i—k bonds; R_{ij}^{e} is the equilibrium length of the i—j bond; the function $f_{ik}(r_{ik})$ is finite, depends on the nature of the interacting atoms, and smoothly decreases to zero at distances longer than ≥2 Å; H_{ij} is the cubic spline which depends on the number of H and C atoms adjacent to the atom i; and δ_i and α_{ijk} are real constants. The second term in formula (2) is a cubic spline which depends on the total number of the atoms adjacent to the i and j atoms ($N_i^{\mathrm{t}}, N_j^{\mathrm{t}}$) and smoothly matches the states with different conjugation types (N_{ij}^{conj}).

The parameters of the potential given by expression (1) were thoroughly optimized[25] to describe the energies and molecular geometries of hydrocarbons with different types of hybridization of the C atoms. Calculations using the potential (1) underestimate (by ~10%) the force constants; however, this drawback is insignificant for the purposes of this work.

Brenner´s potential is widely used for simulation of growth, izomerization, and various structural transformations in fullerenes and CNT including simulation of chemical reactions. This is due to nearly linear increase in computational resources with an increase in the number of particles when solving this type of problems.

The Brenner potential was parametrized over the ground states of molecules. To check its applicability to the description of transition states we preliminarily compared the results of MD simulations with Brenner´s potential and those of *ab initio* (HF/4-31G) calculations of a model reaction $\mathrm{Me}^{\bullet} + \mathrm{H}^{\bullet} \rightarrow \mathrm{CH_4}$. The parameter to be compared was the heat of formation of new C—H bond.

In the *ab initio* approximation, the reaction $\mathrm{Me}^{\bullet} + \mathrm{H}^{\bullet} \rightarrow \mathrm{CH_4}$ was modeled as follows. Assuming a C_{3v} symmetry for $\mathrm{Me}^{\bullet}$ radical we "fixed" the angles of three C—H bonds (θ + 90°) relative to the axis of symmetry, optimized the C—H bond lengths, and then calculated the $E_{\mathrm{Me}^{\bullet}}(\theta)$ energy. For the $\mathrm{CH_4}$ molecule with the same symmetry, we also "fixed" the same three angles (θ + 90°) with respect to the "new" C—H bond, optimized all bond lengths, and calculated the $E_{\mathrm{CH_4}}(\theta)$ energy. The dependence of the energy of the newly formed bond on the angle θ in the strained molecule was calculated as the difference

$$E_{\mathrm{C-H}} = E_{\mathrm{CH_4}}(\theta) - E_{\mathrm{CH_3^{\bullet}}}(\theta) - E_{\mathrm{H}^{\bullet}},$$

where $E_{\mathrm{H}^{\bullet}}$ is the energy of H atom. Analogous calculations were performed by the MD method with Brenner´s potential. In this case, we succeeded in deriving an explicit formula relating the energy $E_{\mathrm{C-H}}$ to the C—H bond length, which allowed the use of analytical optimization procedures.

Results and Discussion

The results of calculations are presented in Fig. 1. Two features engaged our attention. These are, first, linear dependences of the C—H bond energies on the angle θ obtained by both methods and, second, rather close values of the slopes of both straight lines, $\mathrm{d}E/\mathrm{d}\theta$. This suggests that Brenner´s potential allows correct reproduction of the energy characteristics of nonequilibrium structures for at least not too large PA values.

When studying the effect of local strain in a carbon cluster C_n on the reactivity of corresponding atoms, it is of particular interest to consider the segments with nonzero local curvature of the surface. Therefore, we chose the cap of a CNT (a total of 100 atoms), determined the PA values, and then successively attached a radical R ($\mathrm{H}^{\bullet}$ or $\mathrm{Me}^{\bullet}$) to each of the 100 carbon atoms, optimized the geometry, and calculated the heat of corresponding reaction:

$$E = E(\mathrm{C}_n) + E(\mathrm{R}) - E(\mathrm{C}_n\mathrm{R}),$$

where $E(\mathrm{C}_n)$ is the energy of the C_n cluster. These calculations were carried out by the MD method with Brenner´s

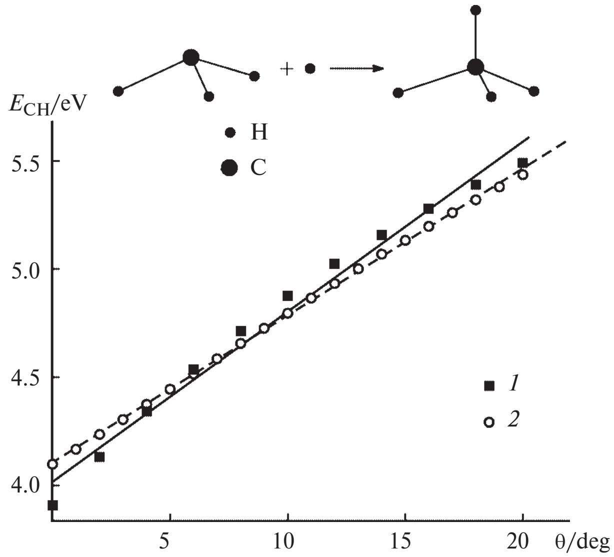

Fig. 1. Bond energy of H atom (E_{CH}) in strained methane molecule calculated using the *ab initio* approach (*1*) and MD simulation with Brenner's potential (*2*). The solid and dashed lines were obtained by linear approximation of corresponding data.

potential while integration of the equations of motion was performed using the Verlet—Beeman algorithm[28] with a MD step of 0.35 fs.

The heat of addition reaction (E) of H atom and Me$^{\bullet}$ radical is a linear function of the PA of the carbon atoms of the CNT (Fig. 2), *i.e.*, $E = c\theta_P + b$. Of course, the heats of corresponding reactions for H atom and Me$^{\bullet}$ radical are different. Depending on the type of a group of three faces that share the reacting carbon atom of the CNT, there are two interpolating straight lines for each addend. The heats of addition to the reacting atom fall on one pair of the interpolating lines if one of the cycles is a pentagon and on the other pair if the reacting atom is shared by three hexagons.

Linear approximations for the two groups of atoms and reagents differ in numerical values of corresponding coefficients, namely, $b_{Me} = 0.65$ and $b_H = 0.85$ eV; $c_{Me}{}^6 = 0.077$, $c_{Me}{}^5 = 0.086$ and $c_H{}^6 = 0.07$, $c_H{}^5 = 0.083$ eV deg^{-1}. The superscript "6" indicates that the reacting atom is shared by three hexagons while the superscript "5" indicates that this atom is shared by at least one pentagon; the subscript denotes the radical. The same values of the b coefficients (0.85 and 0.65 eV) were obtained for the model addition reaction of the reagents to the central atom of a C_{57} fragment of planar graphite sheet.

For the atoms shared by pentagons we also calculated the heats of addition to the "reference" structures (fullerenes C_{20} and C_{60}, where each carbon atom is shared by at least one pentagon). We found rather large differences between the PA values for different atoms (see Fig. 2).

The electronic structure of the cap and the adjacent cylindrical fragment of a CNT capped at one end with an unsymmetrical cap was calculated by the modified tight-binding (TB) method.[29] This approximation uses

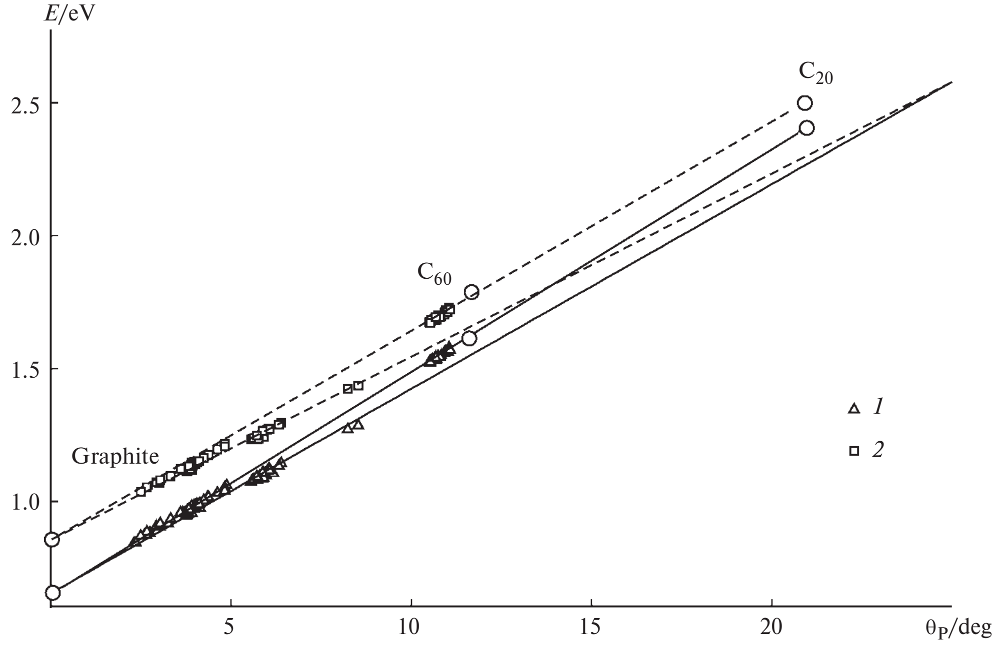

Fig. 2. Heats of addition reactions (E) of Me$^{\bullet}$ radical (*1*) and H atom (*2*) to a CNT, obtained from MD simulations. In each group, the lower line corresponds to the atoms belonging to hexagons only while the upper line corresponds to the atoms belonging to at least one pentagon. The values for the "reference" structures (graphite, C_{20}, and C_{60}) are shown by circles.

the Hamiltonian similar to that used in the EHT calculations with the s—p basis set and special parametrization. The total energy of the system under study is written as the sum of single-electron energies, E_k, over the occupied states

$$U_{\mathrm{el}} = \sum_{k}^{\mathrm{occ}} E_k \tag{4}$$

and repulsive terms

$$U_{\mathrm{rep}} = \sum_{i} \sum_{j>i} \varphi(r_{ij})\,. \tag{5}$$

The function ϕ has the form

$$\phi(r_{ij}) = \phi_0\exp[-\beta(r_{ij} - d_0)],$$

where d_0 is the sum of covalent radii of the interacting atoms. Single-electron energy levels E_n are found[29] by solving the matrix equation

$$(H - E_nS)C^n = 0, \tag{6}$$

where H is the matrix of the Hamiltonian, S is the overlap matrix, and E_n and C^n are the eigenvalues and eigenvectors, respectively. The Hamiltonian was constructed using the Slater—Coster approach which takes into account the dependence of the matrix elements of the Hamiltonian on the direction cosines of the bond vectors. A method proposed recently[29] allows analytical calculations of the first and second derivatives of the total energy with respect to Cartesian coordinates. This makes the MD simulation much faster and facilitates calculations of the Hessian that is necessary for the determination of complete vibrational spectrum of the system under study.

The results of the Mulliken population analysis, obtained in this approximation are shown in Fig. 3 and the Schlegel diagram and the atomic numbering scheme for the cap are presented in Fig. 4.

As can be seen in Figs. 3 and 4, all the 30 atoms characterized by high electron densities (compared to the averaged electron density) belong to six pentagons that determine the curvature of the cap. Increased electron densities makes these atoms more reactive. This seems to be responsible for the difference between their bond energies and those of the atoms of hexagons.

Recently, TB and *ab initio* calculations of the electronic structure of a fragment of carbon surface near the apex of nanocones were reported.[30] The curvature of this surface fragment is determined by one or several pentagons. It was shown that near-Fermi resonant states can be created depending on the number and mutual arrangement of the pentagons. This leads to excess electron density on the constituent atoms the pentagons and should make them more reactive. Such pentagons can favor field emission and serve as probes for tunnel microscopes.

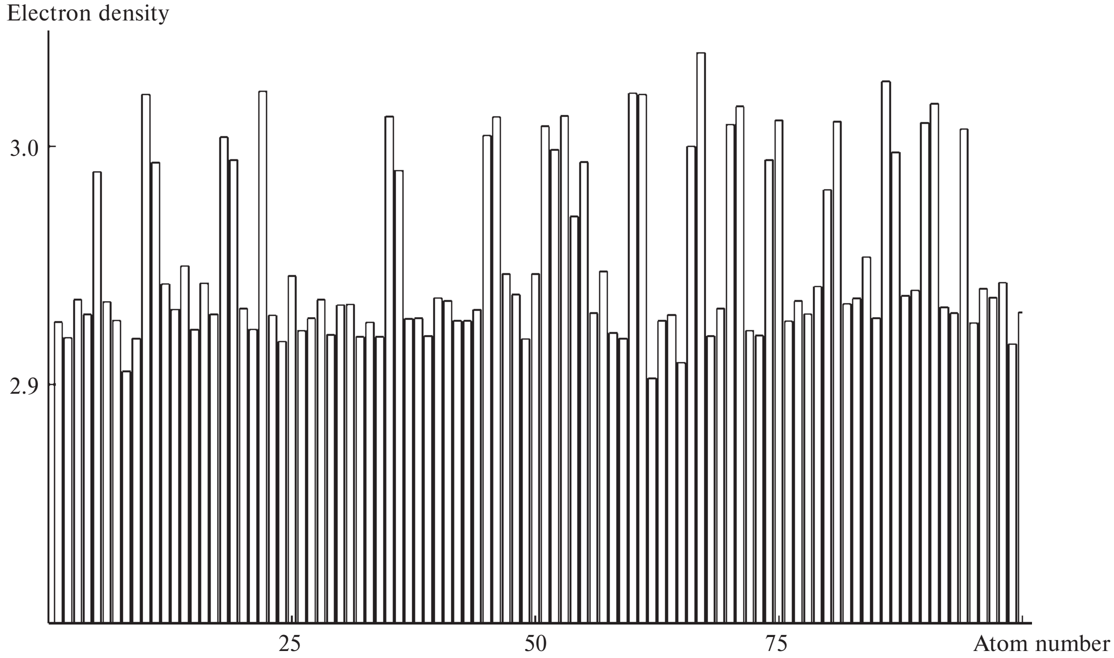

Fig. 3. Partial Mulliken charges of atoms of the cap and adjacent fragment of a CNT in units of electron charge. The atoms characterized by excess electron density (>3e) belong to pentagons.

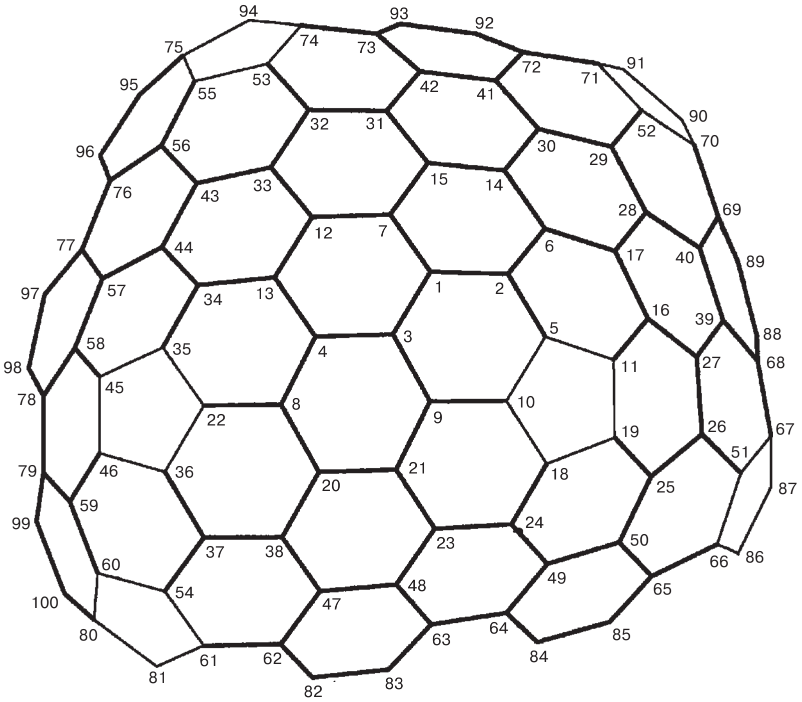

Fig. 4. Schlegel diagram and the atomic numbering scheme for the cap atoms (the atomic numbering scheme is the same as that used in Fig. 3).

* * *

The results obtained in this work show that (i) MD simulations with Brenner´s potential can be useful for studying the effect of the pyramidalization degree of carbon centers in carbon clusters on their reactivity and (ii) the heats of homolytic addition reactions of H atoms and Me$^{\bullet}$ radical to the atoms of curved carbon sheet are linear functions of the pyramidalization angle, which is a geometric parameter introduced as quantitative measure of the local curvature of carbon sheet in the vicinity of a given atom and determining its local electronic properties.

Thus, it is possible to reliably predict the reactivity of carbon clusters (*e.g.*, nanotubes and fullerenes) without performing labor-consuming quantum-chemical calculations.

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