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LETTERS TO THE EDITOR

Influence of the Nanotube Type on the Conformational Behavior of Encapsulated Ethane Molecule

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It is well known that the nanotubes may significantly alter the physicochemical properties of the encapsulated molecules [1–3]. In particular, it has been shown recently that the eclipsed conformation is the most favorable in the case of ethane molecule inside a single-wall carbon nanotube, in contrast to the free ethane molecule with the potential energy minimum corresponding to the staggered conformation [4]. Besides carbon nanotubes, the structurally similar nanosized objects can be built of the boron-nitrogen hexagonal fragments; the latter type of nanotubes attracts attention due to the set of peculiar properties [5]. In this work, the analysis of the conformation of ethane incorporated into two types of model single-wall nanotubes was performed using the DFT PBE/3z method implemented in PRIRODA software package [6]. The model nanotubes parameters were as follows: **I**, $C_{60}H_{12}$ (l = 8.5 Å, d = 4.8 Å) and **II**, $C_{24}B_{18}N_{18}H_{12}$ (l = 8.6 Å, d = 4.7–5.0 Å).

According to the simulation results, in the case of the free ethane molecule the staggered conformation was favorable; however, the method applied underestimated the activation barrier by about 0.5–1.0 kcal mol^{-1} as compared with the experimental values (2.8–3.04 kcal mol^{-1} [7, 8]).

In the course of geometry optimization, ethane molecule inside the nanotube was oriented along the nanotube axis; the conformation of ethane molecule was changed as well.

In the case of the ethane–**I** system (Schemes 1, 2), the smallest distance between ethane hydrogen atoms and the nanotube walls was of 1.7 Å. The partially eclipsed conformer of ethane was the most favorable one (with the angle between the vicinal hydrogen atom bonds of 21.4°–21.5°), and the staggered form corresponds to the transition state. The C–C bond of

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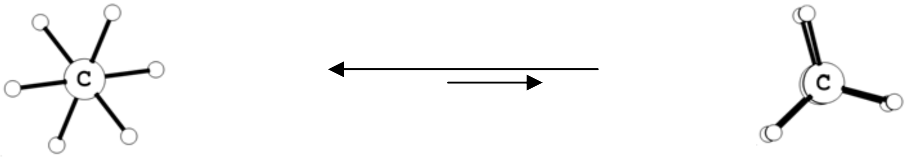
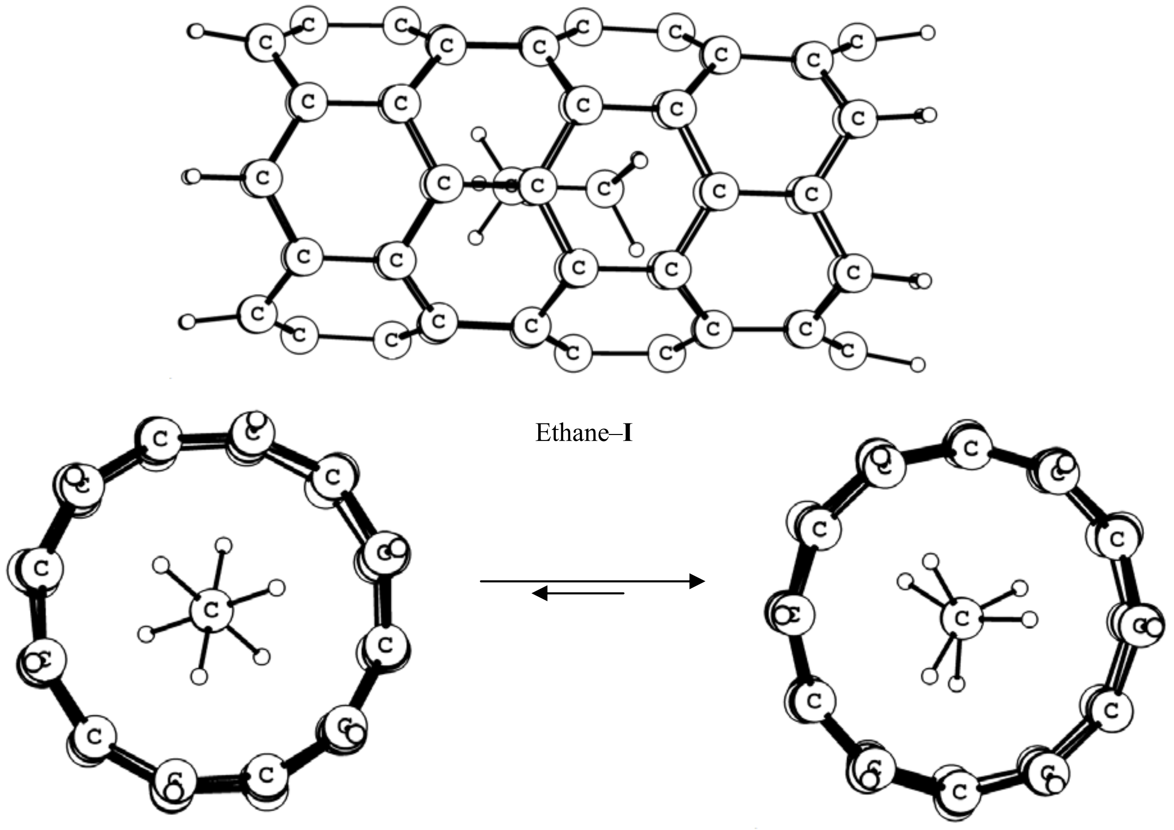
Scheme 1.



Free ethane, staggered form is favorable:
$\Delta H_0^{\neq}$ 2.3 kcal mol^{-1}; $\Delta H_{298}^{\neq}$ 2.0 kcal mol^{-1}; $\Delta G_{298}^{\neq}$ 2.5 kcal mol^{-1}.

Scheme 2.



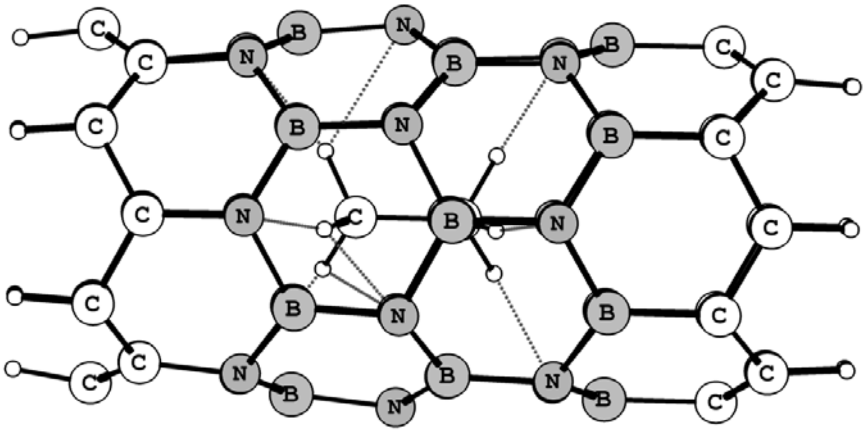
Ethane–**I**

Ethane encapsulated in nanotube I, partially eclipsed form is favorable:
$\Delta H_0^{\neq}$ 1.6 kcal mol^{-1}; $\Delta H_{298}^{\neq}$ 1.4 kcal mol^{-1}; $\Delta G_{298}^{\neq}$ 1.7 kcal mol^{-1}.

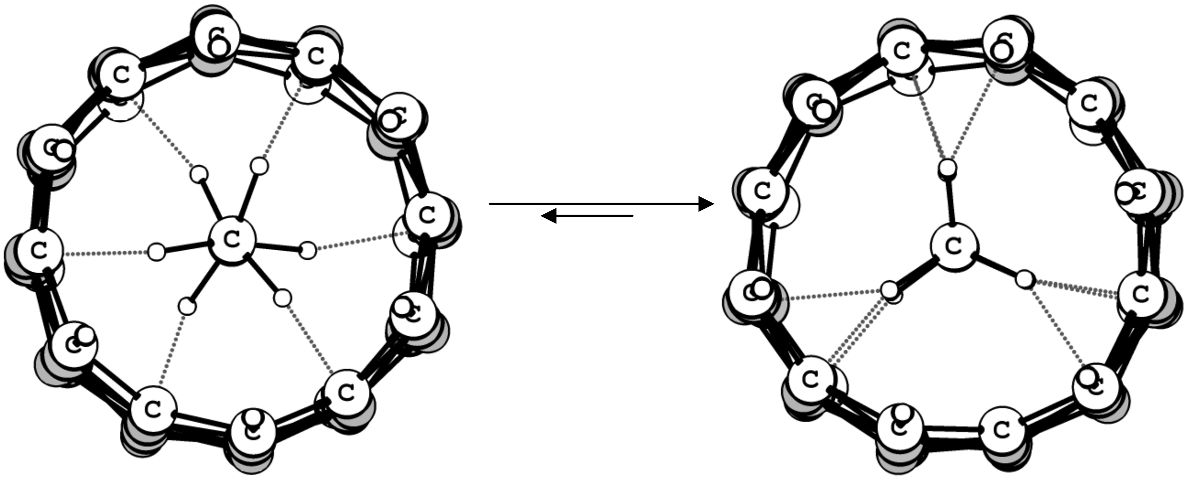
the encapsulated molecule was by 0.112–0.097 Å shorter than that in the free ethane molecule; the C–C bond order was also decreased about twofold upon encapsulation (0.50–0.49 versus 1.0–1.02). The Hessian matrix of the system with the eclipsed conformer did not contain any imaginary frequencies, whereas there was one imaginary frequency in the Hessian of the system containing the staggered form of ethane. As it corresponded to the torsion oscillations around the C–C bond, the staggered conformation could be reliably assigned to the transition state between the two partially eclipsed conformers.

In the case of ethane encapsulated into the nanotube **II** (Scheme 3), the distance between ethane hydrogen atoms and the nanotube wall was similar to that in the ethane–**I** system (1.6–1.8 Å). The completely eclipsed con-formation corresponded to the energy minimum, whereas the staggered conformation was again regarded as the transition state (following the analysis of the imaginary frequencies in the corresponding Hessians). The energy difference between the conformers was lower than that in the case of ethane in the nanotube **I**. In both conformers, supplementary bonds were formed between hydrogen atoms of ethane and the nanotube nitrogen atoms. The C–C bond order (0.66) was lowered, and the bond was by 0.082–0.095 Å shorter as compared with the free ethane molecule. However, the distance between the closest hydrogen atoms in the eclipsed conformer (2.373–2.374 Å) increased as compared with that in the free ethane molecule (2.361 Å).

Scheme 3.



Ethane–**II**



Ethane encapsulated in nanotube II, fully eclipsed form is favorable:
$\Delta H_0^{\ne}$ 0.8 kcal mol^{-1}; $\Delta H_{298}^{\ne}$ 0.5 kcal mol^{-1}; $\Delta G_{298}^{\ne}$ 0.9 kcal mol^{-1}.

The encapsulated ethane molecule was charged in the both studied systems: 0.40 to 0.48 in the case of **I** and –1.15 to –1.22 in the case of **II**, though the ethane–nanotube system as a whole being neutral.

To conclude, the ethane molecule encapsulated inside the nanotube was somewhat "compressed," and its conformation properties were significantly changed.

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