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LETTERS TO THE EDITOR

Theoretical Evaluation of Conformational Preference of the Propane Molecule in Nanotubes

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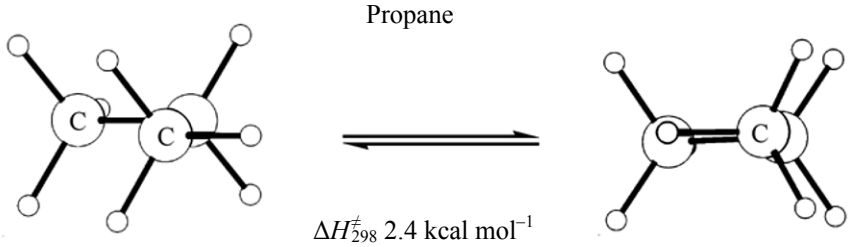
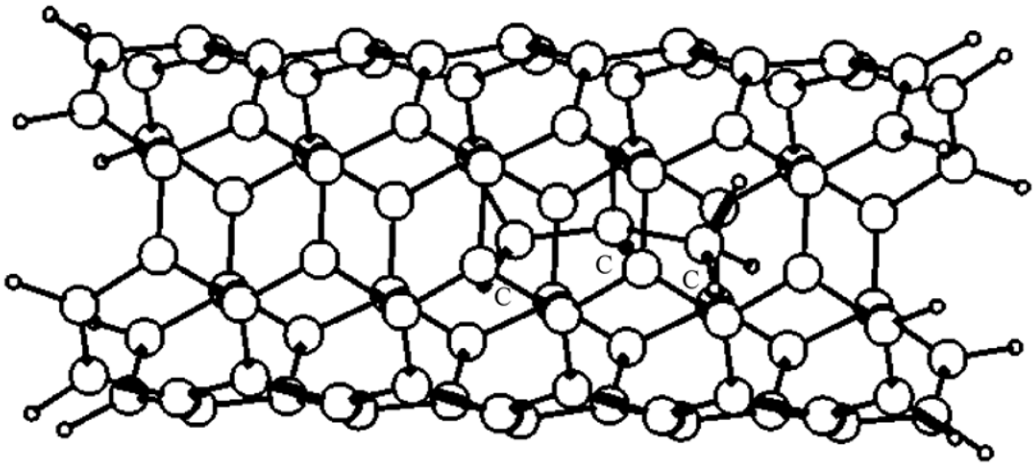
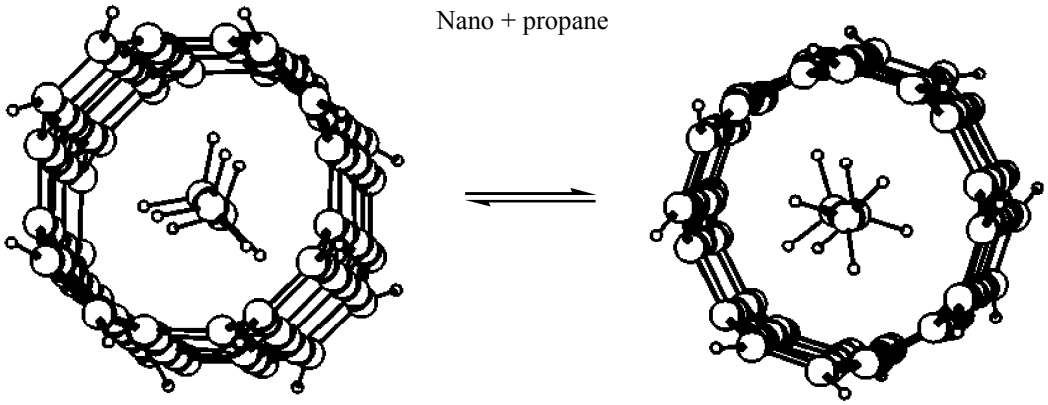
The experimental value of the barrier of hindered rotation in propane ($\Delta H^{\neq}$) is 3.6 kcal mol^{-1} in favor of the staggered conformer [1]. Preference for the staggered form is caused by the mutual repulsion of the valence unbound atoms [1, 2] or the adjacent C–H bonds [3], or is associated with the stabilizing influence of the electronic interactions [4].

Nanotubes are known to have an influence on the physical and chemical characteristics of the encapsulated molecules, and can greatly change the properties of the latter [5, 6]. In this work a conformational analysis of the propane molecule encapsulated into the model single-walled nanotubes [$C_{88}H_{16}$ (**I**), *l* 12.3 Å, *d* 5.6 Å; $C_{96}H_8$ (**II**), *l* 14.1 Å, *d* 5.6 Å] was carried out for the first time using the DFT PBE/3z method (PRIRODA package [7]).

The calculations data for the free propane molecule indicate the relative preference of the staggered form,





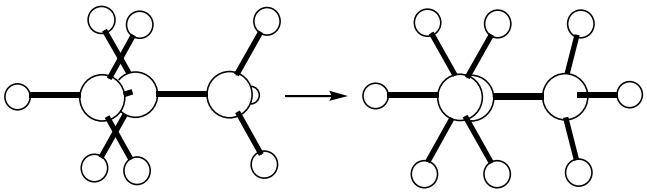


Nano-**I** : $\Delta H^{\neq}_{298}$ 1.2 kcal mol^{-1}

Nano-**II** : $\Delta H^{\neq}_{298}$ 0.3 kcal mol^{-1}

but the value $\Delta H^{\neq}$ is less by 1.2 kcal mol^{-1} compared with the experiment. During the optimization of the geometry of the nanotube–propane system the propane molecule is oriented along the symmetry axis of the nanotube.

For the propane molecule encapsulated into the nanotubes the staggered form is not realized. The completely eclipsed conformer was found to be the most stable. The transition state corresponds to a partial staggered conformation that preserves the eclipsed fragment on one end of the molecule. The relative stability of the eclipsed form reaches 1.2 kcal mol^{-1} (nano-**I**). In this case, compared to the free molecule the calculated length of the C–C bond of the encapsulated forms is reduced by 0.031–0.043 Å, the value of CCC angle increases from 113° to 150°, and the order of the C–C bond decreases from 1.05 to 0.56–0.40. The encapsulated molecule of propane acquires a slight negative charge (from –0.37 to –0.38), although the whole nanotube–propane system is electrically neutral. The distance between the hydrogen atoms of the propane molecule and nanotube wall is 1.9–2.1 Å on the average. In both cases, the Hessian matrix of the system with the partially staggered form of the encapsulated molecule contains one imaginary frequency, which is characteristic of the transition state. The staggered form of propane encapsulated into the nanotubes characteristic for the free molecule was not detected: during the search of the second transition state it was transformed into a partially eclipsed conformation.



At present, it is difficult to identify unambiguously the cause of stabilizing the eclipsed form of propane in the nanotubes. At the same time, the results obtained indicate that within the considered model a kind of force field forms inside the nanotube, which radically changes the conformational preference of even relatively simple molecules.

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