

LETTERS  
TO THE EDITOR

## Theoretical Evaluation of Conformational Preference of the Hexafluoroethane Molecule in Nanotubes

V. V. Kuznetsov<sup>a,b</sup>

<sup>a</sup> Ufa State Aviation Technical University, ul. K. Marksa 12, Ufa, 450000 Russia  
e-mail: kuzmaggy@mail.ru

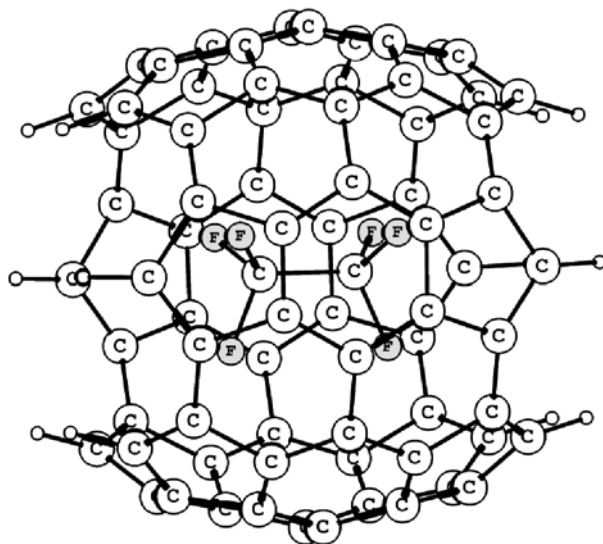
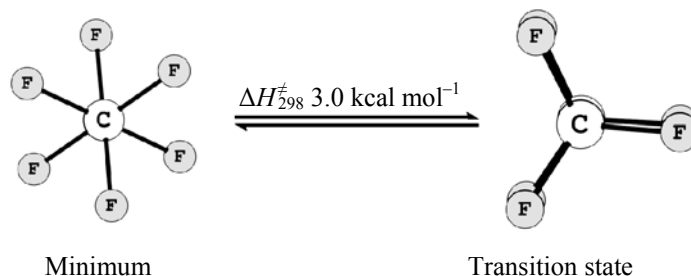
<sup>b</sup> Ufa State Petroleum Technological University, Ufa, Russia

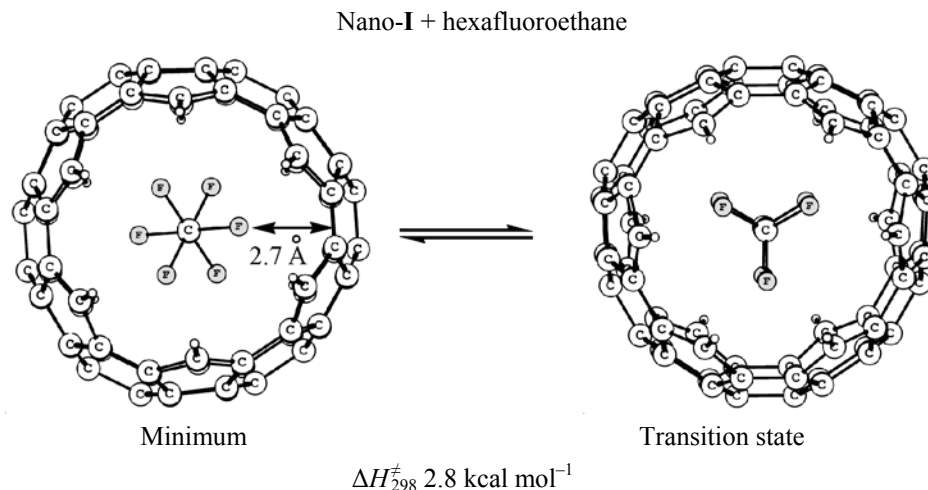
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The experimental value of the barrier of hindered rotation in hexafluoroethane ( $\Delta H^\ddagger$ ) is 3.9–4.4 kcal mol<sup>-1</sup> in favor of the staggered conformer [1, 2]. On the other hand, it is known that nanotubes have an influence on the physical and chemical characteristics of the encapsulated molecules and can greatly change the properties of the latter [3–5]. In particular, recently it has been shown that for ethane encapsulated into nanotube

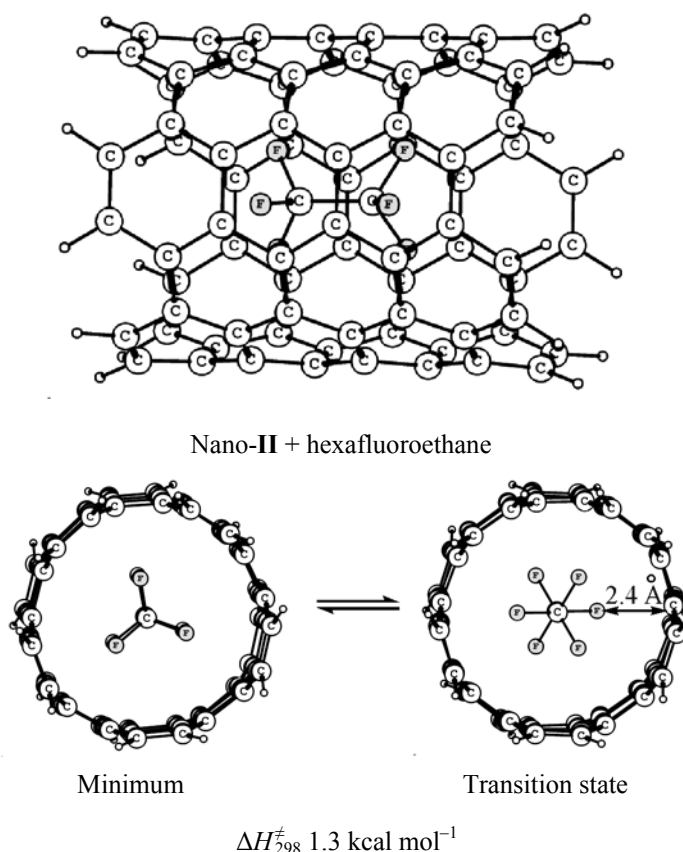
the minimum potential energy of the internal rotation corresponds not to the staggered conformer as for a free molecule, but to the eclipsed conformer [6]. In this work, a conformational analysis of the hexafluoroethane molecule encapsulated into the model single-walled nanotubes [C<sub>72</sub>H<sub>12</sub> (I), *l* 6.6 Å, *d* 5.6 Å; C<sub>80</sub>H<sub>20</sub> (II), *l* 7.4 Å, *d* 6.8 Å] was carried out for the first time using the DFT PBE/3z method (PRIRODA package [7]).





The calculations data for the free hexafluoroethane molecule indicate the relative preference of the staggered form, but the value  $\Delta H^\ddagger$  is by 1.2 kcal mol<sup>-1</sup> less compared with the experiment. During the optimization of the geometry of the nanotube-C<sub>2</sub>F<sub>6</sub> system the hexafluoroethane molecule is oriented along the symmetry axis of the nanotube.

For hexafluoroethane-nano-I system, in which minimal distance between the fluorine atoms and nanotube walls is 2.7 Å, the staggered conformer is more stable. The transition state corresponds to eclipsed conformation. In this case, the calculated value of  $\Delta H^\ddagger$  is a little less than that for the free C<sub>2</sub>F<sub>6</sub> molecule, and the C-C bond in the encapsulated forms is shorter by 0.026–0.028 Å. In the case of nano-II–



hexafluoroethane system characterized by a smaller distance between the fluorine atoms and nanotube walls (2.4 Å), the minimum corresponds to eclipsed form and the transition state, to staggered conformation as in the case of ethane [6]. The length of the C–C bond of both forms is also reduced by 0.013–0.003 Å compared to the free molecule. At the same time the distance between the nearest fluorine atoms in eclipsed conformer increases (2.566–2.570 Å) compared with the free molecule of C<sub>2</sub>F<sub>6</sub> (2.534–2.535 Å). The molecule encapsulated in both nanotubes acquires a small negative charge (from –0.12 to –0.16), although the whole nanotube–hexafluoroethane system is electrically neutral. In both cases, the Hessian matrix of the transition state contains one imaginary frequency.

At present, it is difficult to identify unambiguously the cause of the inversion of the relative stability of staggered and eclipsed forms of the hexafluoroethane molecule in the nano-II. 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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