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LETTERS TO THE EDITOR

Theoretical Evaluation of Conformational Preference of the Ethane Molecule in Fullerene C_{60}

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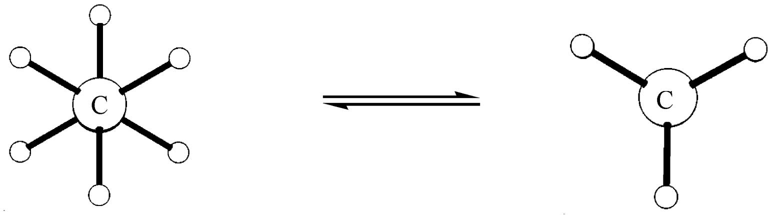
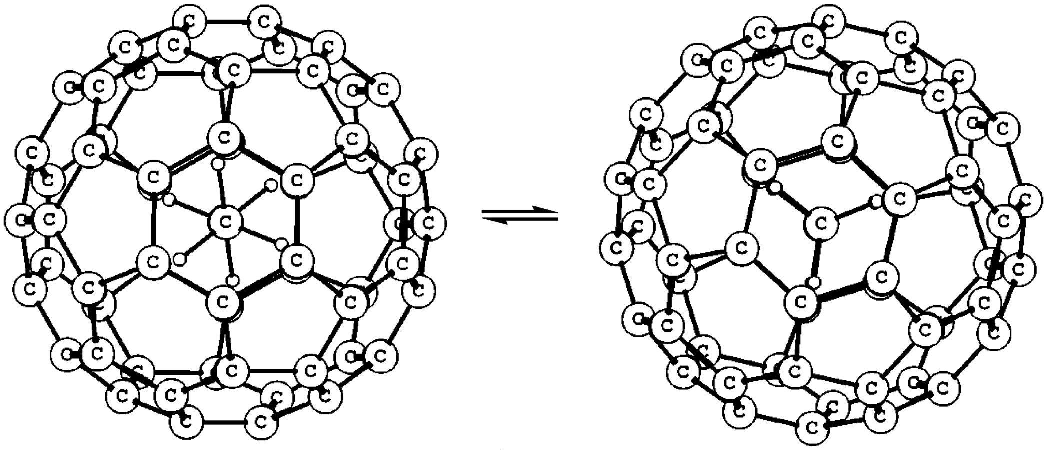
It is known that nano-objects significantly affect the physical and chemical characteristics of the encapsulated molecules and can essentially change the properties of the latter [1]. In particular, earlier we have shown using computer simulation [2] that the inversion barrier of ammonia encapsulated into nanotube increases by 2.5–5.8 times compared with the free molecule. In this work the conformational behavior of the ethane molecules encapsulated into fullerene C_{60} sphere was first investigated using the semi-empirical



0.0

AM1: $\Delta H_0^{\neq}$ 1.3; $\Delta H_{298}^{\neq}$ 0.7; $\Delta G_{298}^{\neq}$ 1.4; $\Delta S_{298}^{\neq}$ –2.2
PM3: $\Delta H_0^{\neq}$ 2.0; $\Delta H_{298}^{\neq}$ 0.8; $\Delta G_{298}^{\neq}$ 1.4; $\Delta S_{298}^{\neq}$ –1.9
PBE/3z: $\Delta H_0^{\neq}$ 2.3; $\Delta H_{298}^{\neq}$ 2.0; $\Delta G_{298}^{\neq}$ 2.5; $\Delta S_{298}^{\neq}$ –1.5



0.0

AM1: $\Delta H_0^{\neq}$ 2.6; $\Delta H_{298}^{\neq}$ 1.9; $\Delta G_{298}^{\neq}$ 1.0; $\Delta S_{298}^{\neq}$ 3.1
PM3: $\Delta H_0^{\neq}$ 2.0; $\Delta H_{298}^{\neq}$ 0.9; $\Delta G_{298}^{\neq}$ 0.6; $\Delta S_{298}^{\neq}$ 0.6
PBE/3z: $\Delta H_0^{\neq}$ 2.9; $\Delta H_{298}^{\neq}$ 2.3; $\Delta G_{298}^{\neq}$ 3.3; $\Delta S_{298}^{\neq}$ –3.3

Energy parameters of internal rotation (kcal mol^{-1}, cal mol^{-1} K^{-1}).

AM1 and PM3 approximations within the software HyperChem [3] and by DFT PBE/3z method (PRIRODA package [4]).

Ethane is characterized by hindered rotation: by spectroscopic data and heat capacity, a potential barrier of transition between the staggered conformers is 2.8–3.04 kcal mol^{-1} [5–8]. Preference for the staggered forms is due to the mutual repulsion of the valence unbound atoms [5, 6] or the adjacent C–H bonds [7], or is a consequence of stabilizing electron interactions in the staggered conformer [8]

The obtained results show that the used computational approaches underestimate the relative stability of staggered conformer of the ethane molecule itself. The data obtained by PBE/3z method are most similar to the experimental data. At the same time, the energy parameters of the internal rotation of ethane encapsulated into fullerene are changed in some way. The staggered form is still more preferable. However, its relative stability increases (AM1 and PBE/3z) compared to the free molecule of ethane ($\Delta H^{\neq}$). Within the latter calculation method, the value of $\Delta G^{\neq}$ increases too. The expected change in entropy as the sign (AM1, PM3) and the absolute value (PBE/3z) is the most notable. According to PBE/3z data, the length of C–C bond reduces significantly in the staggered and eclipsed forms of the encapsulated ethane molecule (1.465 and 1.474 Å) compared to the free molecule (1.531 and 1.544 Å, respectively) and the bond order increases (1.17 and 1.54 for the staggered and eclipsed forms of the encapsulated ethane compared with 1.00–1.02 for the free molecules, respectively). In addition, according to the results of all used computational approximations, both forms of the ethane molecule in the fullerene cavity acquire a small negative charge (from –0.0489 to –0.5117), although in general the system fullerene–ethane is electrically neutral.

Thus, we can assume the formation of a kind of force field inside the fullerene affecting the parameters of the conformational equilibrium of even relatively simple encapsulated molecules.

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