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LETTERS TO THE EDITOR

Nanotube Effect on Conformation of Encapsulated Disilane Molecule

V. V. Kuznetsov[a,b]

[a] *Ufa State Aviation Technical University, ul. K. Marksa 12, Ufa, 450000 Russia*
e-mail: kuzmaggy@mail.ru

[b] *Ufa State Petroleum Technical University, Ufa, Russia*

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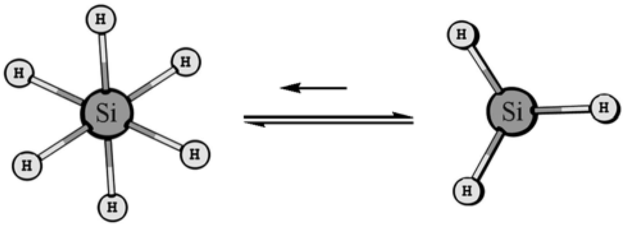
Nanotubes are known to affect physico-chemical parameters of the encapsulated molecules [1]. This opens the possibility of development of novel nanomaterials based on nanotubes containing encapsulated molecules [2]; mechanisms of encapsulation of various substrates have been discussed [3]. Nanosized structures also affect a significant change of conformational properties of molecules encapsulated therein. In particular, it has been demonstrated that the most favorable conformation of ethane in a single-wall carbon nanotube is not staggered (as for the free molecule) but eclipsed [4]. Similar behavior has been revealed in the case of propane [5]. In this work the conformation preferences of disilane molecule inside the model single-wall nanotubes was considered in this work using the PBE/3z hybrid DFT method implemented in the PRIRODA software package [6]. The two nanotubes used in the study were $C_{64}H_{16}$ (**I**) with length of 7.1 Å and diameter of 6.3 Å and $C_{72}H_{12}$ (**II**) with length of 6.6 Å and the highest diameter of 8.4 Å.

Using different computational approximations including the HF and CCSD(T) methods, it has been earlier demonstrated that disilane molecule is characterized by the hindered rotation, and its staggered form is more stable than the eclipsed one [7–9]. This is due to both steric effects [8] and the electrostatic repulsion between the Si–H bonds in the eclipsed form [9]. The simulation of free disilane molecule performed in this work evidenced about the higher relative stability of the staggered form as well. The experimental barrier of the internal rotation in the molecule is of 1.26 kcal/mol according to Raman spectroscopy data [10].

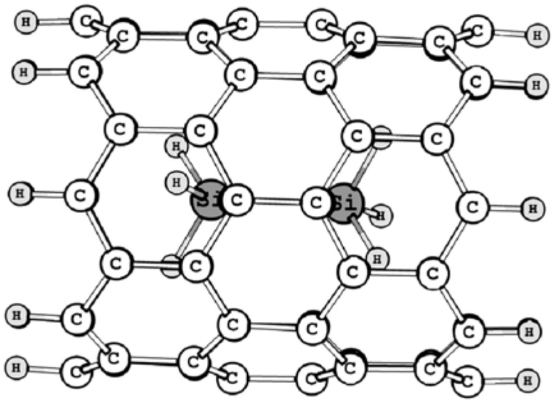


q_{Si} 0.16
q_H –0.05
$\Delta E_0^{\neq} = 0.8$ kcal/mol, $\Delta H_{298}^{\neq} = 0.3$ kcal/mol, $\Delta G_{298}^{\neq} = 1.3$ kcal/mol

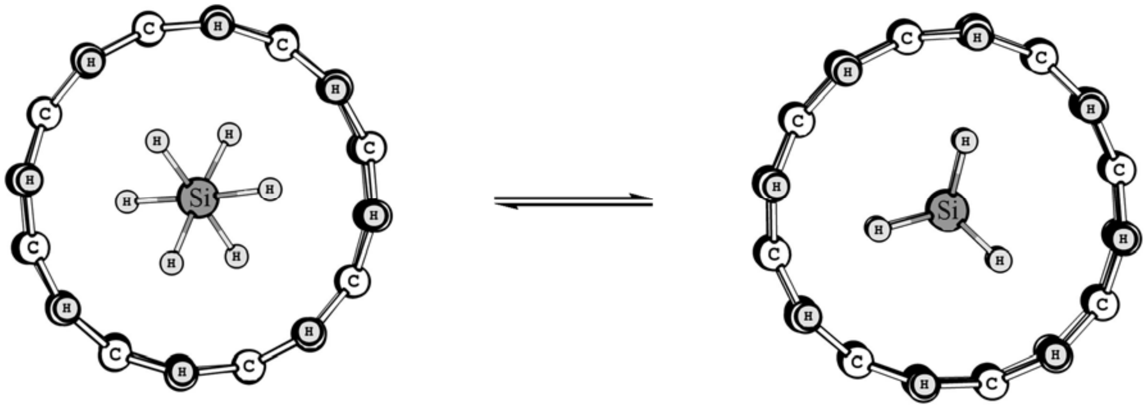
The positive charge was localized at silicon atoms, and the negative charge was localized at hydrogen atoms.

In the case of the system of disilane in the nanotube **I** (with the minimum distance between the hydrogen atoms and the nanotube of 2.2 Å) staggered and eclipsed conformations revealed practically identical energies.

Nano-**I** + Si_2H_6



q_{Si} 0.28; q_H –0.30 to –0.34



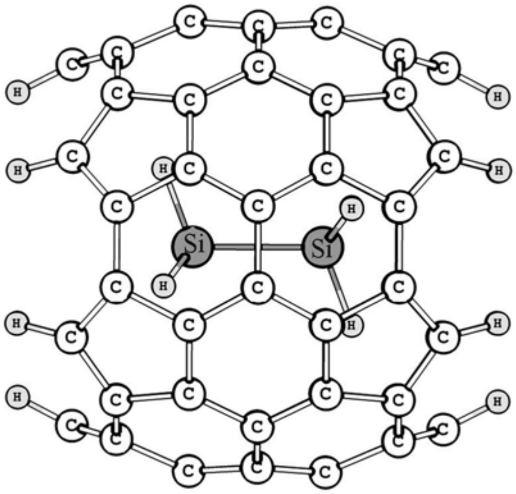
$\Delta E_0^{\neq} = 0.0$ kcal/mol
$\Delta H_{298}^{\neq} = 0.02$ kcal/mol
$\Delta G_{298}^{\neq} = 0.0$ kcal/mol

$\Delta E_0^{\neq} = 0.05$ kcal/mol
$\Delta H_{298}^{\neq} = 0.0$ kcal/mol
$\Delta G_{298}^{\neq} = 0.4$ kcal/mol

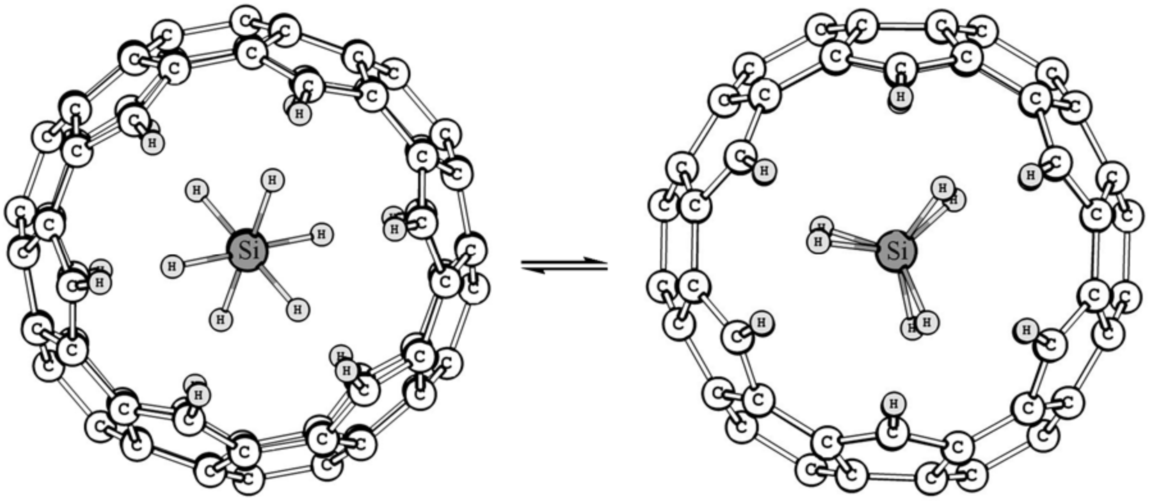
The Si–Si bond length of encapsulated forms of disilane is increased by 0.071–0.045 Å in comparison with the free molecule; the distance between hydrogen atoms in the eclipsed form was increased as well (by 0.25–0.36 Å). The Si–Si bond order (1.15–1.16) was increased as compared to the free Si_2H_6 molecule (1.0–0.98). Apparently, that was due to the charge transfer from the nanotube walls to the disilane molecule: the negative charge at the hydrogen atoms significantly increased in encapsulated forms, and the Si_2H_6 molecule became negatively charged (–1.41 and –1.38 units for the staggered and the eclipsed forms, respectively), however the system with the nanotube as a whole remained neutral.

In the case of the disilane cluster with the nanotube **II**, the distance between hydrogen atoms from the nanotube walls was higher (2.5 Å), and the energy minimum of the encapsulated molecule (except for the $\Delta H_{298}^{\neq}$ value) corresponded to the staggered conformer.

Nano-**II** + Si_2H_6



q_{Si} 0.39
q_H –0.22 to –0.23



$\Delta E_0^{\neq} = 0.0$ kcal/mol
$\Delta H_{298}^{\neq} = 0.07$ kcal/mol
$\Delta G_{298}^{\neq} = 0.0$ kcal/mol

$\Delta E_0^{\neq} = 0.8$ kcal/mol
$\Delta H_{298}^{\neq} = 0.0$ kcal/mol
$\Delta G_{298}^{\neq} = 1.7$ kcal/mol

The Si–Si bond in the latter case was 0.049–0.046 Å shorter than that in the free molecule, and the distance between hydrogen atoms in the eclipsed form was close to those in the free molecule (3.36–3.37 Å). Besides that, the Si–Si bond order (1.21–1.24) in this case is also higher than in the free molecule of disilane. At the same time, the negative charge of disilane molecule is less than in the cluster with nanotube-**I** and is equal to –0.59 and –0.60 for staggered and eclipsed forms respectively. Probably the charge transfer to the hydrogen atoms of disilane in the last case becomes more weak owing to the increase of nanotube diameter; as a result the negative charge at hydrogen atoms becomes less than the positive charge at the silicon atoms by reference to the cluster with nanotube-**I**.

Thus the data of the computer simulation show that the force field of the nanotube considerably affects the conformational preference of encapsulated molecule.

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