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LETTERS TO THE EDITOR

Conformation of Hydroxyborane Encapsulated within Nanotubes

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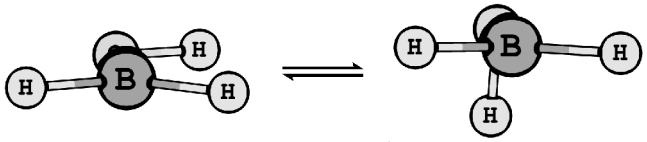
Nanotubes are known to influence the physicochemical parameters of the encapsulated molecules; properties of the latter may significantly differ from those of the free molecules [1–3]. In particular, it has been demonstrated recently that the eclipsed conformation is the favorable one in the case of ethane molecule inside the carbon nanotube, in contrast to the free ethane molecule with the favorable staggered conformation [4]. In this work, the PBE/3z DFT method (PRIRODA package [5]) was applied to study the barrier of internal rotation around the B–O bond in hydroxyborane H_2BOH encapsulated within model single-wall nanotubes: $C_{48}H_{12}$ (7.1 Å long and 4.6 Å in diameter, **I**) and $C_{72}H_{12}$ (6.6 Å long and 8.4 Å in diameter, **II**) (see Schemes 1–3).

The simulation of free hydroxborane revealed that the planar conformation was relatively favorable in that case, its B–O bond (1.362 Å) being shorter than that in the case of the orthogonal form (1.368 Å). The PBE/3z simulation result gave the value of barrier of rotation around B–O bond close to the experimental one measured in the cases of substituted hydroxybonanes (8.5–13.8 kcal/mol [6]). The B–O bond order was of 1.29 in the case of planar hydroxyborane form and 1.18 in the case of orthogonal form.

When hydroxyborane molecule was encapsulated into nanotube **I**, its planar conformation corresponded to the potential energy minimum as well; however, the difference between the forms energy was 3.7–5 times lower than in the case of the free molecule. Hessian of the encapsulated orthogonal H_2BOH contained one imaginary frequency. The B–O bond length was significantly decreased (1.343 Å, the planar form and 1.371 Å, the orthogonal form) whereas its order was increased (1.62, the planar form and 1.78, the orthogonal form). Hence, in the case of nanotube **I** the molecule encapsulating did not invert the relative stability of the conformations (like it happened in the case of ethane [4]); however, the rotation barrier around the B–O bond was significantly lowered.

With the increasing of nanotube diameter, the above-discussed effect almost vanished due to larger

Scheme 1.

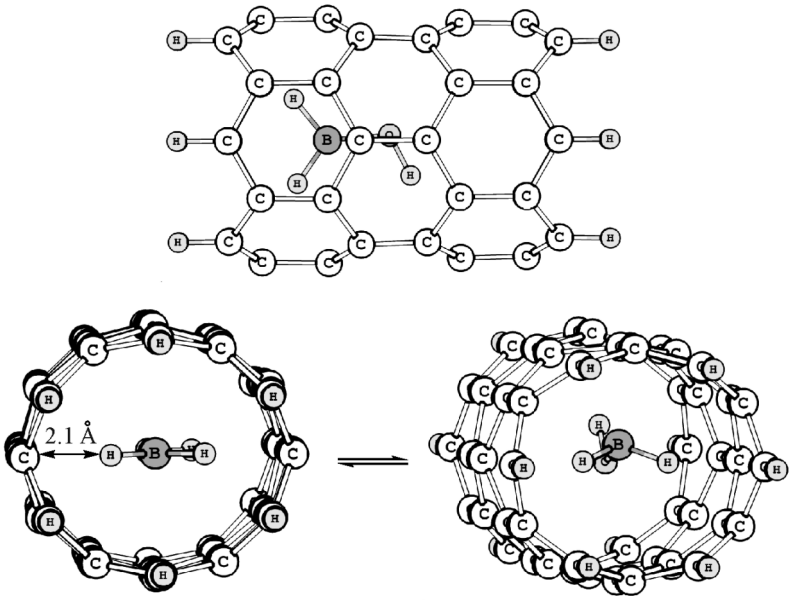


Free hydroxyborane

Planar form Orthogonal form

$\Delta H_0^{\neq}$ 13.9 kcal mol^{-1}; $\Delta H_{298}^{\neq}$ 13.9 kcal mol^{-1}; $\Delta G_{298}^{\neq}$ 13.9 kcal mol^{-1}.

Scheme 2.

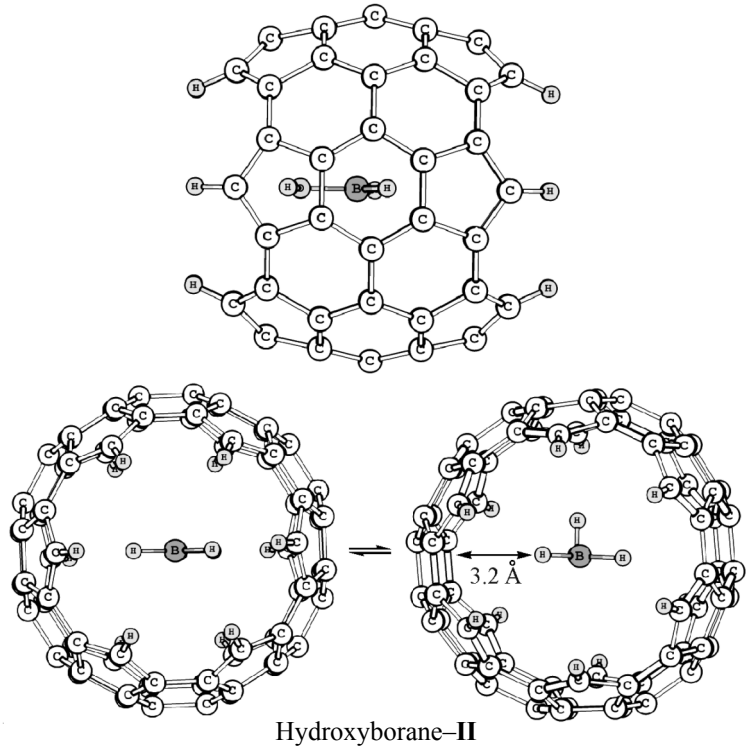


Hydroxyborane–**I**

Planar form Orthogonal form

$\Delta H_0^{\neq}$ 3.0 kcal mol^{-1}; $\Delta H_{298}^{\neq}$ 2.8 kcal mol^{-1}; $\Delta G_{298}^{\neq}$ 3.8 kcal mol^{-1}.

Scheme 3.



Hydroxyborane–**II**

Planar form Orthogonal form

$\Delta H_0^{\neq}$ 13.2 kcal mol^{-1}; $\Delta H_{298}^{\neq}$ 13.2 kcal mol^{-1}; $\Delta G_{298}^{\neq}$ 13.4 kcal mol^{-1}.

distance between the encapsulated molecule and the nanotube wall. In the case of hydroxyborane encapsulated within nanotube **II**, the energy difference between the conformations were close to that of the free molecule, the same applied to the B–O bond length (1.359 Å, the planar form and 1.362 Å, the orthogonal form) and its order (1.18, the planar form and 1.07, the orthogonal form).

The encapsulated hydroxyborane molecule is charged in the both studied systems: 0.43 to 0.55 in case of **I** and –0.12 to –0.14 in case of **II**, although the overall hydroxyborane-nanotube system is electrically nutral.

Thus the data of the computer simulation show that in case of relatively small diameter of nanotube the encapsulated molecule is "compressed" by the force field of the nanostructure; this action leads to the considerable change in its conformational behavior.

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