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LETTERS TO THE EDITOR

Conformational Behavior of 1,3,2-Dioxaborinane Molecule Encapsulated in Fullerenes

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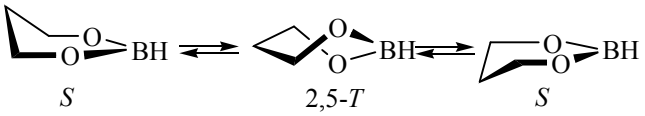
Nanoobjects are known to have a substantial effect on the properties of encapsulated molecules [1]. In particular, using the method of computer simulation, it was recently shown that the barrier to internal rotation of the ethane molecule in fullerene C_{60} as compared to the free molecule ($\Delta H^{\neq}$), depending on the method of calculation, increases 1.1–2.7 times [2], whereas the barrier to inversion about the C–O bond in the methanol molecule encapsulated in nanotube, vice versa, decreases several times [3]. In the present paper the conformational behavior of the molecule of cyclic boron ester: 1,3,2-dioxaborinane **I** – placed inside the cage of fullerenes C_{60} and C_{80} was studied at the DFT (PBE/3z) level (PRIRODA package [4]).

Ester **I** at room temperature is characterized by degenerated interconversion of the two invertomers in the *sofa* conformation (*S*) via the transition state having the 2,5-*twist*-conformation (2,5-*T*) with the barrier to inversion of 7–8 kcal/mol [5] (Scheme 1).

The results of calculations of the isolated molecule of 1,3,2-dioxaborinane (**I**) are close to the experimental data ($\Delta E_0^{\neq}$, $\Delta H_{298}^{\neq}$, $\Delta G_{298}^{\neq}$ in kcal/mol; $\Delta S_{298}^{\neq}$ in cal mol^{-1} K^{-1}). The B–O bond order ($P_{B–O}$) is 1.21 in the *sofa* conformer and 0.92 in the 2,5-*T*-conformer.

The molecule of ester **I** placed into the cage of fullerene C-80 during the geometry optimization is converted from the *sofa* conformation into a flattened

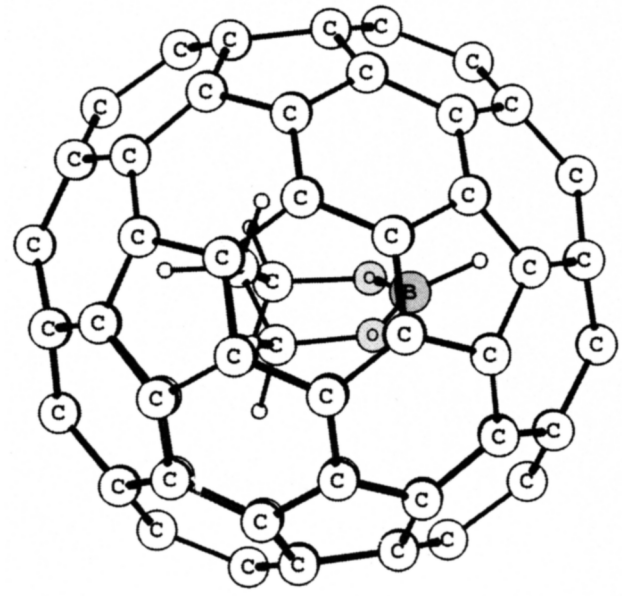
Scheme 1.

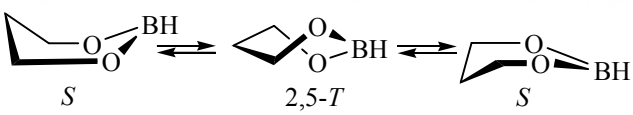


$\Delta E_0^{\neq}$ 7.2 kcal/mol, $\Delta H_{298}^{\neq}$ 6.9 kcal/mol,
$\Delta G_{298}^{\neq}$ 7.2 kcal/mol, $\Delta S_{298}^{\neq}$ –0.8 cal mol^{-1} K^{-1}

Scheme 2.

C-80 + 1,3,2-Dioxaborinane

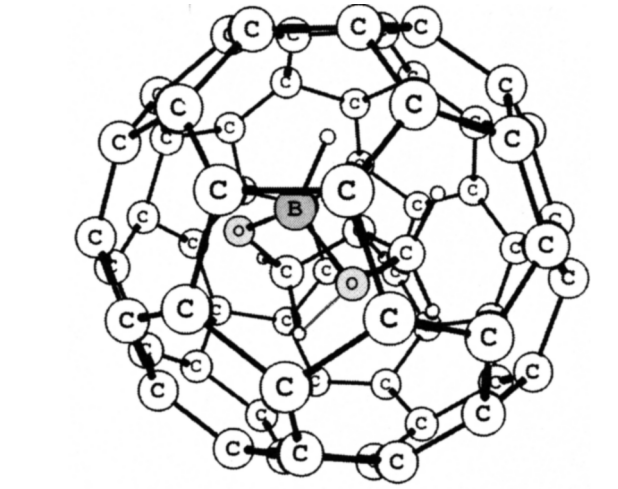




$\Delta E_0^{\neq}$ 9.0 kcal/mol, $\Delta H_{298}^{\neq}$ 8.2 kcal/mol,
$\Delta G_{298}^{\neq}$ 10.1 kcal/mol, $\Delta S_{298}^{\neq}$ –6.4 cal mol^{-1} K^{-1}

Scheme 3.

C-80 + 1,3,2-Dioxaborinane



1,4-*T* TS *C*

0.0 $\Delta E_0^{\neq}$ 27.7 kcal/mol, ΔE_0 8.3 kcal/mol,
$\Delta H_{298}^{\neq}$ 27.5 kcal/mol, ΔH_{298}^{0} 8.4 kcal/mol,
$\Delta G_{298}^{\neq}$ 27.9 kcal/mol, ΔG_{298}^{0} 8.1 kcal/mol,
$\Delta S_{298}^{\neq}$ –1.0 cal mol^{-1} K^{-1} ΔS_{298}^{0} 1.2 cal mol^{-1} K^{-1}

symmetrical boat (*SB*). Its inversion also occurs via the 2,5-*T* transition state but the barrier of this process as compared with the free molecule of ester **I** increases. Also, the B–O bonds become slightly different: $P_{B–O}$ is 1.24 and 1.26 in conformer *SB*, and 1.17 and 1.24 in the 2,5-*T*-form. Besides, the encapsulated molecule **I** acquires negative charge (–0.7397 in the form *SB* and –0.7373 in the form 2,5-*T*) (Scheme 2).

Even more drastic conformational changes occur for ester **I** placed into a smaller in size cage of fullerene C-60. In this case, the *sofa* conformer during the geometry optimization is transformed into the 1,4-*twist* (1,4-*T*) form, corresponding to the global minimum on the potential energy surface, which is never realized for the isolated molecule of this compound [5]. This conformer can be converted by the ring inversion into another minimum, *chair* (*C*), via the transition state (TS) close to the *sofa* conformation (Scheme 3).

Note that conformer *C* is 8.1–8.4 kcal/mol higher in energy that the *twist* form, and the barrier to transition 1,4-*T* → *C* is 3.9 times higher than that calculated for the free molecule of ester **I**. The B–O bond order is notably increased and equals 1.38 and 1.59 for conformer 1,4-*T* and 1.42 and 1.44 for conformer *C*. The encapsulated molecule **I** bears a substantial positive charge: 2.5323 (1,4-*T*), 2.7294 (*C*) and 2.5619 (TS).

Therefore, the force field inside fullerenes significantly affects the conformational behavior of simple cyclic systems and may result in the formation of new conformers, which cannot be realized for the free molecule.

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