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LETTERS TO THE EDITOR

Theoretical Evaluation of Conformational Preference of the 2,2,3,3-Tetramethylbutane Molecule in Nanotubes

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 Technological University, Ufa, Russia

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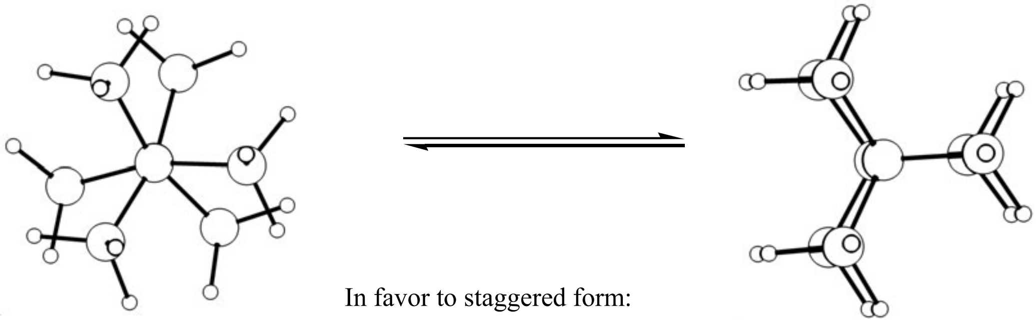
Experimental value of the barrier of hindered rotation around the carbon–carbon bond in ethane molecules and its symmetrically substituted analogs is 3–6 kcal mol^{-1} in favor of the staggered form [1–3]. On the other hand it is known that the nanotubes have an effect on the physical and chemical characteristics of the encapsulated molecules and can essentially change the properties of the latter [4–6]. In particular, recently it was shown that for ethane encapsulated into the nanotube the potential energy minimum of the internal rotation corresponds the eclipsed conformation, but not the staggered form as in a free molecule [7].

In this work the rotation barrier around the central carbon–carbon bond in the 2,2,3,3-tetramethylbutane molecule encapsulated into the model single-walled nanotube $C_{80}H_{20}$ (l 7.4 Å, d 6.8 Å) was studied using semiempirical AM1 and TNDO approximations within the software HyperChem [8] and by the DFT PBE/3z method (PRIRODA package [9]).

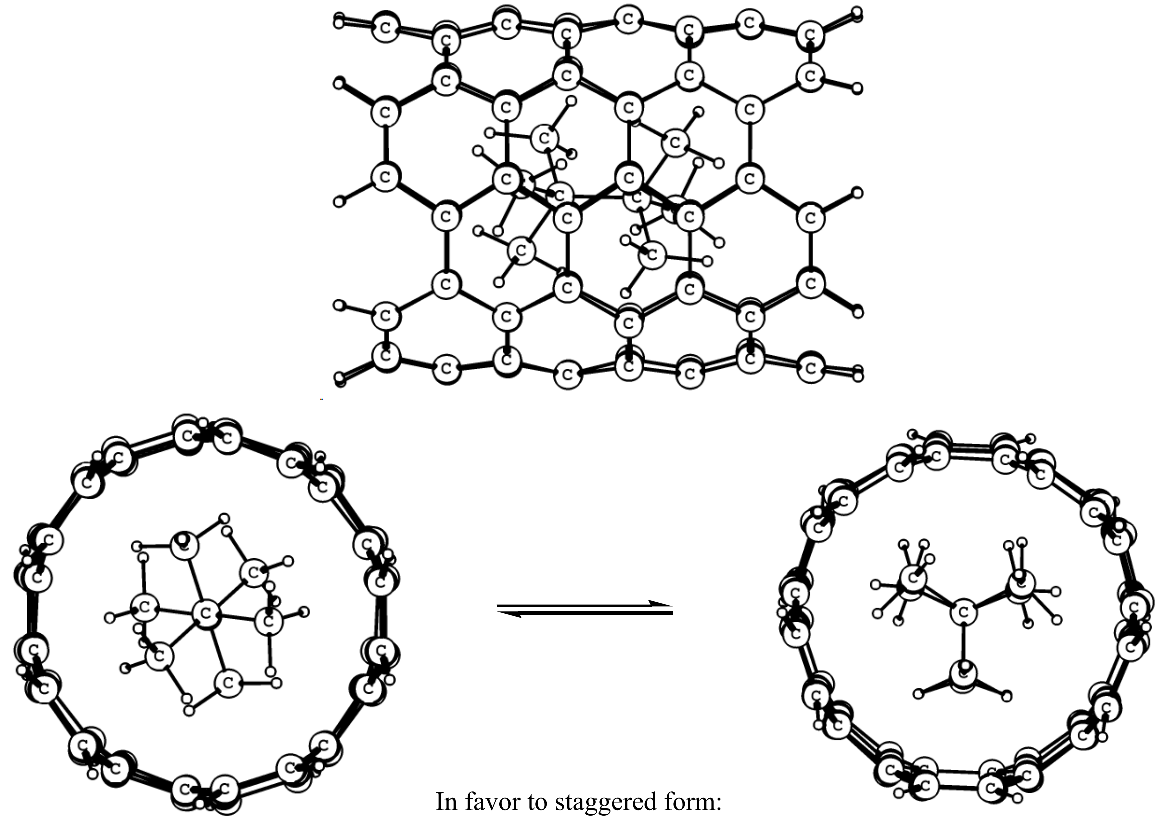
Calculations data for the free hexamethylethane molecule indicate the relative preference of the staggered form, which is characterized by a shorter central C–C bond (by 0.003–0.037 Å) compared with the eclipsed conformation. The results of the PBE/3z method (1.590 Å) are the most close to the experimental data (1.582 Å [10]). According to the optimal geometry, the minimal distance between the hydrogen atoms of the encapsulated molecule and nanotube wall is 1.8–2.0 Å.

Within the calculation approximations AM1 and TNDO, in the case of the hexamethylethane molecule encapsulated into the nanotube the staggered form still corresponds to a minimum, but the height of the potential barrier is significantly lowered. At the same time, according to the PBE/3z method, the eclipsed conformer is the most stable, as in the case of ethane [7]. In this regard, the calculated length of the central C–C bond of the encapsulated molecule reduces by 0.002–0.068 Å compared with the free molecule in both forms. Its order (PBE/3z) decreases from 0.94–0.98 to 0.72–0.26. The encapsulated molecule acquires a slight negative (AM1, PBE/3z) or positive (TNDO) charge (0.1–0.8), although in general the system nanotube–hexamethylethane is electrically neutral.



In favor to staggered form:

AM1: $\Delta H_0^{\neq}$ 5.1 kcal mol^{-1}; $\Delta H_{298}^{\neq}$ 4.8 kcal mol^{-1}; $\Delta G_{298}^{\neq}$ 6.5 kcal mol^{-1}
TNDO: $\Delta H_0^{\neq}$ 7.1 kcal mol^{-1}; $\Delta H_{298}^{\neq}$ 6.8 kcal mol^{-1}; $\Delta G_{298}^{\neq}$ 7.2 kcal mol^{-1}
PBE/3z: $\Delta H_0^{\neq}$ 7.6 kcal mol^{-1}; $\Delta H_{298}^{\neq}$ 6.9 kcal mol^{-1}; $\Delta G_{298}^{\neq}$ 8.6 kcal mol^{-1}.



In favor to staggered form:

AM1: $\Delta H_0^{\neq}$ 3.0 kcal mol^{-1}; $\Delta H_{298}^{\neq}$ 2.1 kcal mol^{-1}; $\Delta G_{298}^{\neq}$ 3.4 kcal mol^{-1}
TNDO: $\Delta H_0^{\neq}$ 0.4 kcal mol^{-1}; $\Delta H_{298}^{\neq}$ 0.3 kcal mol^{-1}; $\Delta G_{298}^{\neq}$ 0.9 kcal mol^{-1}.

In favor to eclipsed form:
PBE/3z: $\Delta H_0^{\neq}$ 1.3 kcal mol^{-1}; $\Delta H_{298}^{\neq}$ 2.2 kcal mol^{-1}; $\Delta G_{298}^{\neq}$ 0.9 kcal mol^{-1}.

According to AM1 results, the Hessian matrix of the system with the staggered form of the encapsulated molecule contains one imaginary frequency, which is characteristic of the transition state. At the same time, according to the TNDO method, the Hessian of both forms contains no imaginary frequencies. In case of PBE/3z calculations, the Hessian of the eclipsed form contains one imaginary frequency corresponding to the rotation of the t-C_4H_9 fragment.

At present, it is difficult to identify unambiguously the cause of stabilizing the eclipsed form of the encapsulated hexamethylethane. At the same time, the results obtained indicate that within the considered model a kind of force field forms inside the nanotube, which changes radically conformational preference of even relatively simple molecules.

REFERENCES

1. Dashevskii, V.G., *Konformatsii organicheskikh molekul* (Conformations of Organic Molecules), Moscow: Khimiya, 1974.
2. Korol'kov, D.V., *Teoreticheskaya khimiya* (Theoretical Chemistry), Moscow: IKTs "Ackadem-Kniga," 2007, vol. 1, p. 226.
3. *Internal Rotation in Molecules*, Orville-Thomas, W.J., Ed., New York: Willey Interscience, 1975.
4. D'yachkov, P.N., *Uglerodnye nanotrubki: stroeniye, svoistva, primeneniye* (Carbon Nanotubes: Structure, Properties, and Use), Moscow: BINOM, Laboratoriya Znanii, 2006.
5. Kuznetsov, V.V., *Zh. Obshch. Khim.*, 2012, vol. 82, no. 11, p. 1931.
6. Kuznetsov, V.V., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 1, p. 140.
7. Kuznetsov, V.V., *Zh. Org. Khim.*, 2013, vol. 49, no. 2, p. 319.
8. *HyperChem 8.0*. http://www.hyper.com.
9. Laikov, D.N. and Ustynyuk, Yu.A., *Izv. Akad. Nauk, Ser. Khim.*, 2005, no. 3, p. 804.
10. Bartell, L.S. and Boates, T.L., *J. Mol. Struct.*, 1976, vol. 32, no. 2, p. 379.