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LETTERS TO THE EDITOR

Theoretical Evaluation of Inversion Barier of Trimethylamine in Nanotubes

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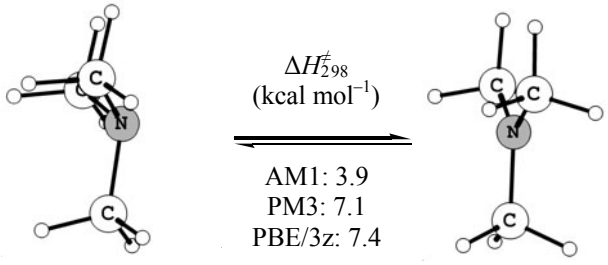
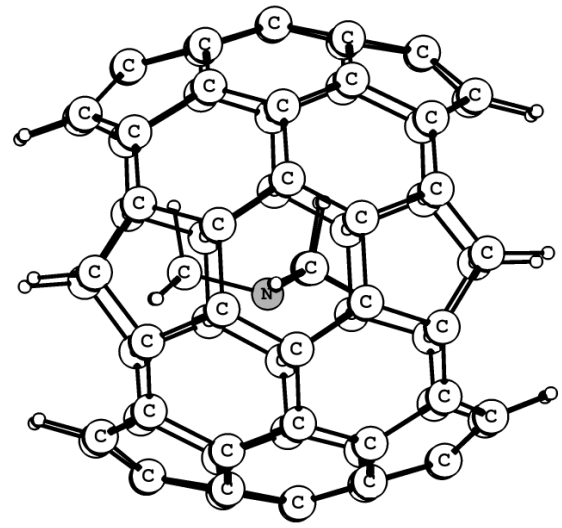
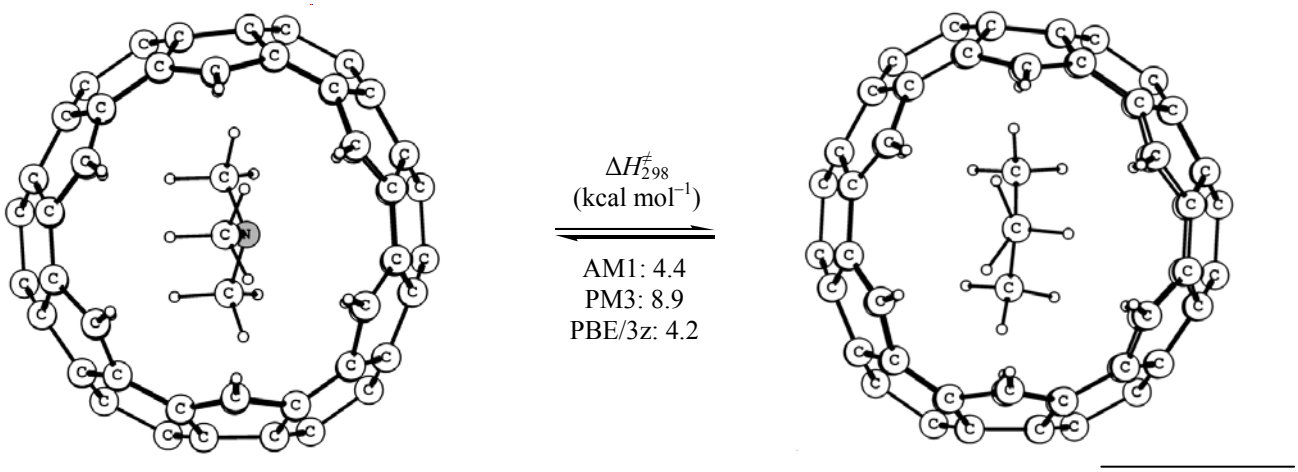
Nanotubes are known to have an influence on the physical and chemical characteristics of the encapsulated molecules, and can greatly change the properties of the latter [1]. In particular, earlier we have shown using computer simulation [2] that the inversion barrier of ammonia encapsulated into nanotube increases 2.5–5.8 times compared with the free molecule. In this work the inversion barrier of the nitrogen atom of the trimethylamine molecule encapsulated into the single-walled nanotube $C_{72}H_{12}$ (*l* 6.6 Å, *d* 8.3 Å) was studied using semiempirical AM1 and PM3 approximations within the software HyperChem [3] and by the DFT PBE/3z method (PRIRODA package [4]).

Experimental value of the barrier to inversion of the nitrogen in trimethylamine ($\Delta H^{\neq}$) is 8.2 kcal mol^{-1} [5]. The calculation data on trimethylamine itself show that all the used computational approaches underestimate the value of $\Delta H^{\neq}$ by 0.8–4.3 kcal mol^{-1}. When the $(CH_3)_3N$ molecule was initially placed into the nanotube, their symmetry axis coincided. However, during optimization of the geometry of this system the amine nitrogen atom turned to the nanotube wall, and the symmetry axes became perpendicular. In the optimized system, the shortest distance of the hydrogen atoms of trimethylamine from the nanotube walls is 2.5–2.7 Å on the average.

According to the semiempirical approximations, the calculated value of pyramidal inversion of the encapsulated molecules is 1.1–1.3 times higher than in the absence of nanotubes. On the contrary, by the results of the PBE/3z method this value 1.8 times decreases. In this case, the C–N bonds of both forms become shorter than in the free molecule by 0.01–0.002 Å. The amine acquires low negative charge







(according to the approximation PBE/3z, –0.5036 and –0.3319 for the ground and transition states, respectively). In general, the system nanotube–amine is electrically neutral. In all the used approximations the Hessian matrix of the system with the planar form of the encapsulated molecule contains one imaginary frequency, which is characteristic of the transition state.

As in the case of ammonia [2], the results obtained indicate that within the considered model a kind of force field forms inside the nanotube, which changes dynamic parameters of even relatively simple molecules.

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