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LETTERS TO THE EDITOR

Theoretical Evaluation of Relative Stability of Diazadifluoride Isomers in Nanotubes

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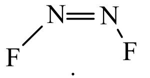
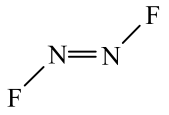
It is known that nanotubes affect physical and chemical characteristics of the encapsulated molecules and, in principle, can significantly change the properties of the latter [1]. In this work, we first investigated the relative stability of the molecules of *cis*- and *trans*-isomers of diazadifluoride (difluorodiazene) inside the single-wall nanotubes [$C_{52}H_8$ (**I**), with length and diameter of 8.8 and 5.5 Å, respectively, and $C_{81}H_{12}$ (**II**), with length and a diameter of 6.6 and 8.4 Å, respectively] using AM1 and PM3 semi-empirical approximations within the HyperChem software [2] and PBE/3z DFT-method (PRIRODA package [3]).

The calculation results of diazadifluoride confirm the experimental data [4] on the greater stability of the *cis*-isomer molecules. A detailed analysis of the



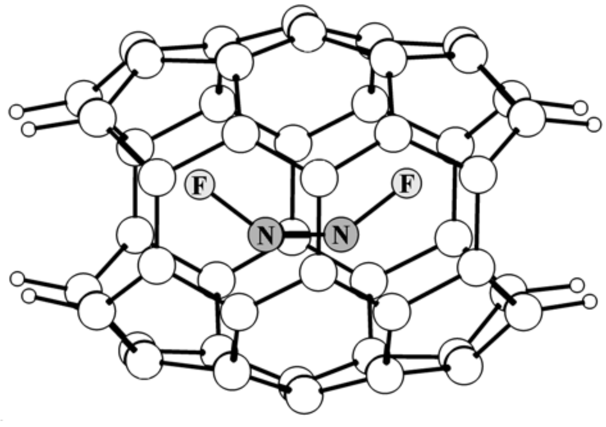
cis-

ΔG^0_{298} 0.0 kcal mol^{-1}



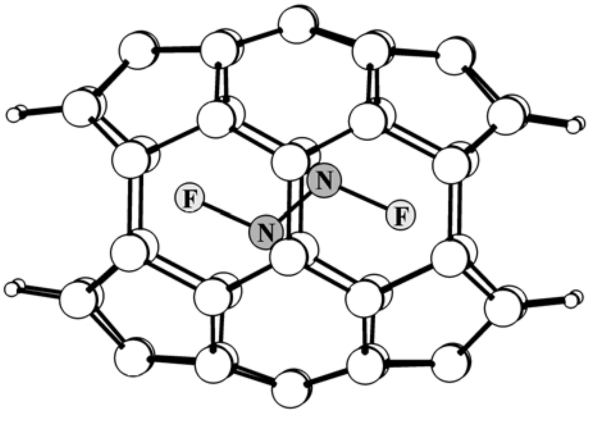
trans-

AM1: 10.4 kcal mol^{-1}
PM3: 1.4 kcal mol^{-1}
PBE/3z: 3.4 kcal mol^{-1}



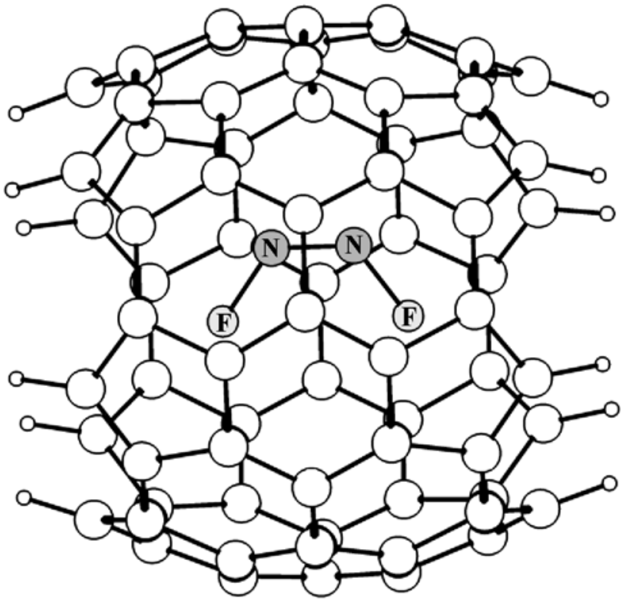
nano-**I** + *cis*-

AM1: 26.3 kcal mol^{-1}
PM3: 35.5 kcal mol^{-1}
PBE/3z: 27.4 kcal mol^{-1}



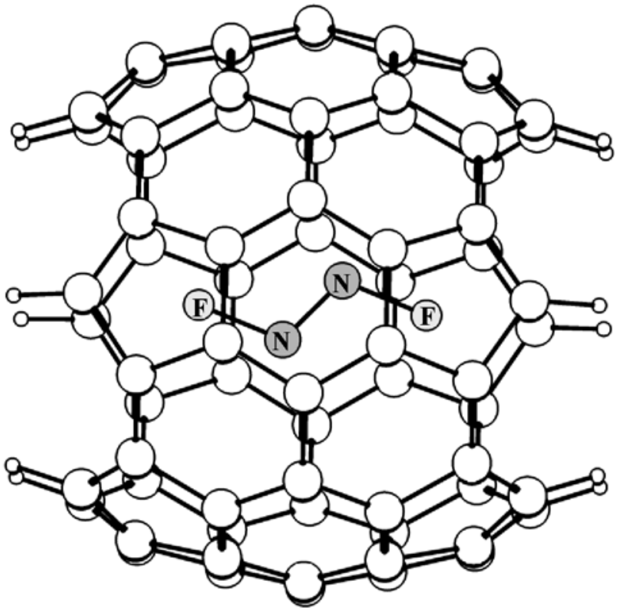
nano-**I** + *trans*-

0.0 kcal mol^{-1}



nano-**II** + *cis*-

AM1: 0.0 kcal mol^{-1}
PM3: 2.0 kcal mol^{-1}
PBE/3z: 0.0 kcal mol^{-1}



nano-**II** + *trans*-

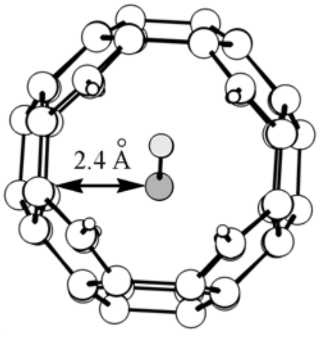
AM1: 9.2 kcal mol^{-1}
PM3: 0.0 kcal mol^{-1}
PBE/3z: 3.6 kcal mol^{-1}

reasons for this is presented in [5]. However, the relative stability of the isomers of the compound placed inside the nanotubes varies considerably depending on their diameter.

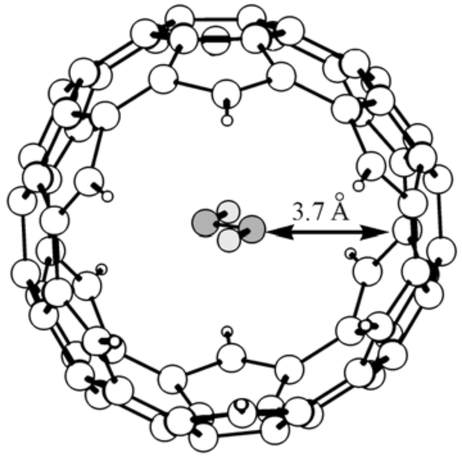
As the result of geometry optimization of “nanotube-N_2F_2” system the molecule of diazadifluoride was located along the longitudinal symmetry axis of the nanotube.

In the case of the structure of nano-**I** the *trans*-form is the most stable, and its relative stability is greater than the energy difference of the free diazadifluoride molecules. For a system with nano-**II**, which is characterized by a significant distance between the nitrogen atoms of difluorodiazene and the tube walls, the relative stability of the *trans*-isomer decreases (PM3) or, as in the free N_2F_2 molecules, is less than the *cis*-form (AM1, PBE/3z).

The whole nanotube–difluorodiazene system is electrically neutral. However, the encapsulated molecule has a slight electrical charge. According to



nano-**I** + *cis*-



nano-**II** + *trans*-

PBE/3z method, in the case of nano-**I** it varies from –0.2414 (*cis*) to –0.2928 (*trans*), and for nano-**II**, from –0.0245 (*cis*) to –0.0035 (*trans*).

At the present time it is difficult to establish the unambiguous reason of the inversion of the relative stability of *cis*-and *trans*-isomers of diazadifluoride placed in the nanotube. We can only mention a certain dependence of the energy of geometric isomers of N_2F_2 on the N=N bond length established in [5]: a decrease of this value of 0.002 Å leads to a greater increase in the stability of this form. The result of this study for the free diazadifluoride molecule (PBE/3z, 0.015 Å in favor of the *cis*-form) confirms this conclusion. For the encapsulated molecules the discussed bond length (PBE/3z) decreases by 0.003 Å in the *trans*-form for nano-**I** and by 0.015 Å in the *cis*-isomer (as in the case of the free N_2F_2 molecule) for nano-**II**. Thus, the changes in the N=N bond length allows to explain in a first approximation the observed stabilization of the *trans*-isomer molecules in a system with nano-**I** and its absence in the case of nano-**II**.

These results indicate the formation of a force field in the nanotube that can significantly change the structural and energy parameters, even of relatively simple molecules.

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