Stabilization of small nitrogen clusters via spatial constraint

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Abstract. We apply density functional theory to calculate activation barriers for dissociations of small all-nitrogen clusters N_4 and N_6. The effect of external spatial constraint was also considered. We found that spatial constraint results in significant stabilization of both regarded clusters. So, the spatial constraint can be considered as an efficient method for stabilization of high-energy nitrogen structures.

1. Introduction

Non-molecular forms of nitrogen are considered as promising fuels and energy sources. They can decompose into N_2 molecules, releasing large amounts of energy. N_2 molecules present in the Earth's atmosphere and are therefore safe for the environment. In addition, non-molecular forms of nitrogen can store more energy per unit mass in comparison with traditional fuels.

Beyond earlier predicted [1] and synthesised [2] solid forms of non-molecular nitrogen, all-nitrogen clusters were also actively investigated [3-7]. Among the clusters considered, the smallest are N_4 and N_6 cages. Despite their small sizes and high-strained skeletons, these systems possess moderate kinetic stability. The measure of such stability is the activation barrier, which separate cluster from two (for N_4) or three (for N_6) nitrogen molecules. For N_4 tetrahedral molecule, the corresponding barrier achieves about 280 kJ/mol [8-9]. At the same time, the value of 30 kcal/mol (equal to 126 kJ/mol) is considered as a minimal barrier acceptable for the potential use of the cluster [10].

Additional stabilization of nitrogen clusters (in particular, small clusters N_4 and N_6) can provide their wide utility. One possible strategy is the introduction of carbon atoms into nitrogen skeleton. Many carbon-nitrogen structures were proposed in recent years [11-13]. They have higher stability than pure nitrogen systems, but they are much less stable in comparison with carbon cages [14-15]. In addition, the presence of carbon or other elements can result in toxic products of the system's decomposition.

Here we investigate another strategy based on the special constraint of considered clusters. Constraints can be realized inside larger clusters or pores as well as under high pressures. It's well known that constraint can not only increase, but also decrease the stability of small clusters. For example, the activation energy for decomposition of hydrocarbon tetrahedrane is about 0.66 eV [16], whereas the same value for tetrahedrane encapsulated inside C_{60} fullerene is only 0.33 eV [17]. This is why we perform a detailed investigation of the influence of constraint on the stability of nitrogen clusters.

2. Materials and Methods

To study nitrogen clusters, we apply density functional theory with the Becke's hybrid exchanged-corrected functional B3LYP [18-19] coupled with the electron basis set of 6 -31G* [20]. The energy barriers were calculated as the energy differences between stable and transition geometries of considered clusters. The transition states geometries were confirmed by hessian calculations: all of them had only one imaginary frequency.

To simulate special constraints, we adobe method proposed in Ref. [21]. We add additional term E_{add} in the system's energy:

$$E_{add} = \sum_{i=1}^{N} k r_i^2$$

Here $n = 4$ or 6 is the number of atoms in considered cluster, k is the fitting parameter (its value depends on concrete realization of spatial constraint), r_i is the distance between i-th atom and cluster's center of mass. First and second derivatives of E_{add} contribute to atomic forces and the Hessian matrix, respectively. We extracted atomic forces and Hessian matrix from the GAMESS program package [22], added to it additional terms and calculated atomic displacements and frequencies spectrum with our homemade code. Common Newton-Raphson approach was used to locate equilibrium and transition states.

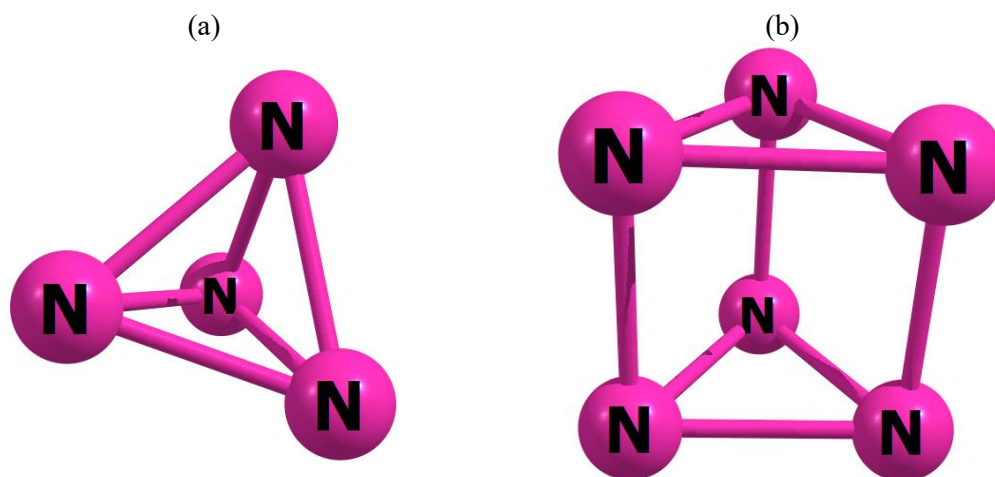Considered N_4 and N_6 clusters are presented in Figure 1.

Figure 1. Atomic structures of considered nitrogen clusters N_4 (*a*) and N_6 (*b*).

3. Results and Discussions

We calculate the activation barriers for N_4 (*a*) and N_6 clusters as functions of coefficient k. This coefficient provides tuning of "rigidity" of the applied constraint. Its actual value depends on the interaction of nitrogen clusters with their environment. Endohedral system C60@Nn, in which nitrogen clusters are encapsulated into fullerene cage, is one of possible realization considered in Ref. [23]. Other schemes, for example with larger fullerenes, are also possible.

The dependence of activation barriers on k is presented in Figure 2. One can see that, in contrast to hydrocarbon tetrahedrane, the stability of nitrogen clusters increases under constraints. We observed a monotonic increase of the activation barrier with k. The values of activation barriers can exceed 3 eV and 2 eV under constraint for N_4 and N_6 clusters, respectively. According to Arrhenius low, reaction rates depend exponentially on the barrier height. So, an increase of the barrier by 0.1 eV leads to a fifty-fold decreasing of the decomposition rate at room temperature.
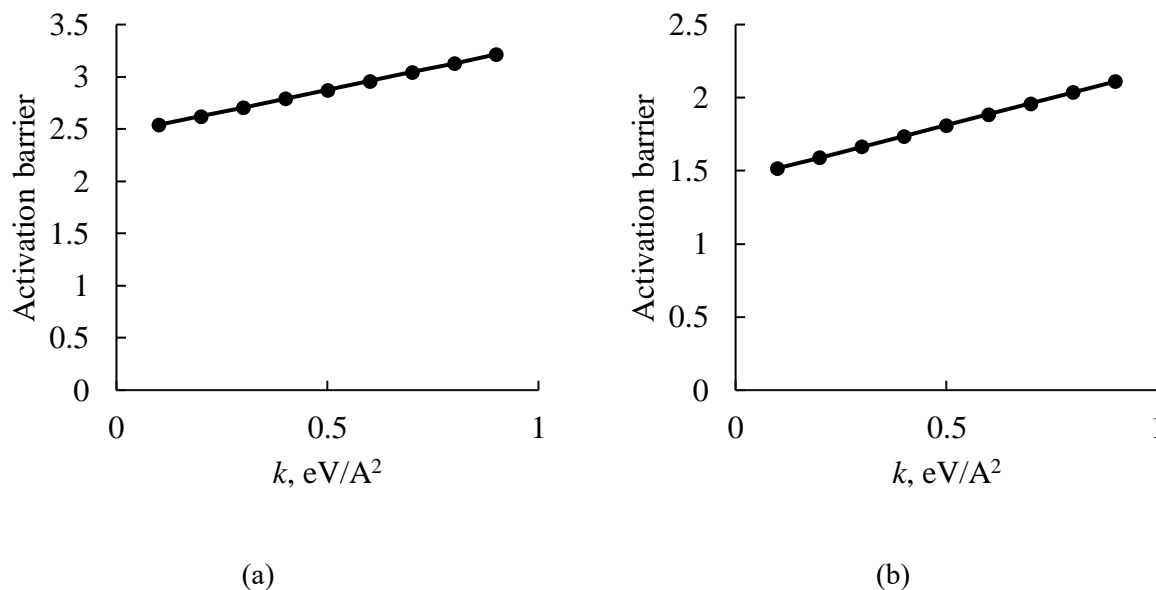
(a)   (b)

Figure 2. The dependence of activation barriers on k values for N_4 (a) and N_6 (b) clusters under spatial constraint.

4. Conclusions

Small nitrogen clusters N_4 and N_6 possess very high kinetic stability. The activation barrier for their decompositions to nitrogen molecules are much higher than that for similar hydrocarbon clusters C_4H_4 and C_6H_6 and even for larger hydrocarbon systems (for example, prismanes [24], tetracubyl [25], etc.). Moreover, they are more stable than common high-energy CL-20 cage [26-27]. Spatial constraint provides an efficient way for further increase of their stabilities. Under constraints, both N_4 and N_6 clusters can preserve their structures even at high temperatures. We believe that this basic investigation can stimulate further search of all-nitrogen high-energy density materials with low sensitivity based on small nitrogen clusters.

5. Acknowledgements

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