Thermal Stability of Heptaprismane $C_{14}H_{14}$

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Abstract. Heptaprismane has been numerically simulated by the method of the nonorthogonal tight-binding model in this paper. Thermokinetic parameters of its decomposition (activation energy and the frequency factor) have been determined. The temperature dependence of the heptaprismane lifetime in the temperature range $T = 300 - 1000\text{K}$ has been investigated. Obtained data have been compared well with the earlier reported results concerning the "smaller" polyprismanes.

1. Introduction

Quantum chemical calculations are the powerful tools for design and investigation of new hypothetical molecules and nanostructures. So, new class of carbon molecules with a half-flat configuration of carbon atoms was recently designed [1]. These molecular systems are refer to as the carbon [n, m]prismanes or polyprismanes, where *m* is the number of vertices of a closed carbon ring, and *n* is the number of layers of dehydrogenated cycloalkane molecules [2]. There are problems with synthesis of the rings because of the technical difficulties arising at construction of them [2]. Therefore only some types of "small" prismanes, such as [2, 3]prismane, [2, 4]prismane, cubane [3], and [2, 5]prismane [4] have been obtained. Electronic properties and structural characteristics of the [n, m]prismanes have been actively studied in the density functional theory for the last time [5,6,7]. Their electronic characteristics were studied in detail for possible using of polyprismanes in nanoelectronics as a nanoconductors [8]. The mechanical properties of polyprismanes were actively studied as well. For example there was investigated the influence of edge doping with different atoms and functional groups on mechanical characteristics of the samples [9,10]. Existence of negative Poisson's ratio in these molecular systems has been also established [11]. Nevertheless, despite the great interest to polyprismanes, the problem of obtaining even "small" prismanes remains unsolved. A detailed study of their thermal stability is able to solve this problem. To date, the the following structures were already investigated: cubane C_8H_8 [12], hexaprismane $C_{12}H_{12}$ [13] and octaprismane $C_{16}H_{16}$ [13]. However, it is necessary to investigate structures consisting of an odd number of carbon atoms for a more detailed study of this problem. In that context, one of the most interesting system for consideration is the polyprismane $C_{14}H_{14}$ (Fig. 1) that occupies an intermediate position between $C_{12}H_{12}$ and $C_{16}H_{16}$. In this paper, we simulate the dynamics of heptaprismane $C_{14}H_{14}$ thermal decomposition in a wide temperature range. From obtained data we can determinate the thermal stability of a structure and to estimate the lifetime of the sample at different temperatures. Activation energy E_a and frequency factor A are also derived.

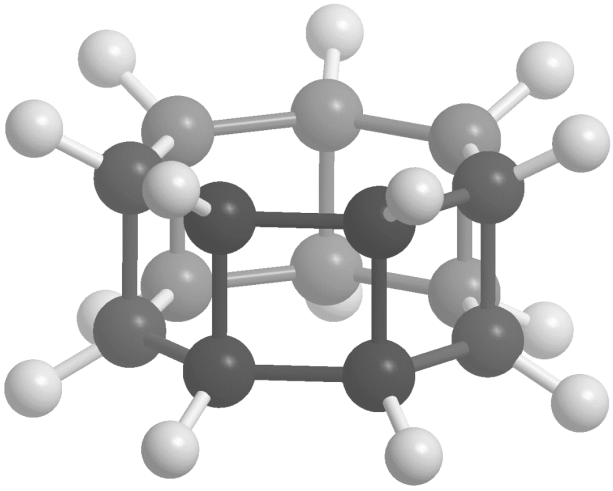

Fig. 1. Heptaprismane $C_{14}H_{14}$. Dark balls are carbon atoms, and light balls are hydrogen atoms.

2. Computational details

All quantum-mechanical calculations were carried out by GAMESS software complex [14] in terms of the DFT with the B3LYP hybrid exchange-correlation potential [15,16] and basis 6-311G as well as the use nonorthogonal tight-binding model [17] with appropriate parameters set [18]. As was pointed in recent studies [12], the model given admits the partition of total potential energy on two parts: electronic orbital and ion repulsive energy. This method matches well with structural and energetic characteristics every one of small hydrocarbon molecules and macroscopic systems. The advantage over an *ab initio* methods is higher computer performance that allows an exploration the evolution of the system with ~100 atoms within 1 ns to 1 μs – it's quite enough to obtain a statistical data. Earlier the same model was successfully applied to molecular dynamic studies of similar high-strained hydrocarbons: hexa- and octaprismane [13], cubane [12], its derivatives [19,20] and tetrahedrane [21]. The equilibrium structures and decomposition products of heptaprismane were obtained by structural relaxation where an initial configuration of the molecule under the influence of internal forces passed to states corresponding to the global or local minimum of the energy. The molecular dynamics simulation was carried out to trace back the temporal evolution of the molecule at high temperatures in the frame of the tight-binding potential [18]. The values of velocity and displacement for all atoms of heptaprismane at the initial time were randomly specified so that total momentum and total angular momentum of the system were zero. Forces acting between atoms were calculated with the Hellmann–Feynman theorem. After this step, classical Newton equations were solved using velocity Verlet method (fast integration method) with a time step of 0.3 fs. Total energy of the cluster consists of potential energy of the system and the sum of kinetic energies of its atoms. During the cluster thermal evolution, total energy of the system remains constant. As an analogue of the usual temperature, a microcanonical temperature T was introduced, which is the measure of the kinetic energy of the relative atomic motion. The value of T was calculated by formula:

$$\langle E_{kin} \rangle = (1/2) k_B T (3N - 6), \quad (1)$$

where $\langle E_{kin} \rangle$ is the time-averaged kinetic energy of the cluster, k_B is the Boltzmann's constant and N = 28 is number of atoms in the heptaprismane.

The atomic coordinates of the molecule were written to analyze the intermediate configurations arising during the evolution of heptaprismane. After the calculation, the computer visualization of the process was carried out.

3. Results and discussion

The binding energies of the heptaprismane molecule, its isomers, and the decomposition products were calculated by the equation:

$$E_b = \left(nE\left(\mathrm{C}\right) + mE\left(\mathrm{H}\right) - E\left(\mathrm{C_{14}H_{14}}\right)\right) / \left(n+m\right), \tag{2}$$

where n=14 and m=14 are the numbers of carbon and hydrogen atoms, respectively, $E(\mathrm{C})$ is the energy of isolated carbon atoms, $E(\mathrm{H})$ is the energy of isolated hydrogen atoms and $E(\mathrm{C_{14}H_{14}})$ is the total energy of the heptaprismane.

The binding energies of heptaprismane in terms of the nonorthogonal tight-binding model [18] is 4.517 eV/atom. This result agrees well with data found using the density functional method (B3LYP/6311G [22]): 4.63 eV/atom. Thermal stability of heptaprismane is determined by the activation energy. Due to the fact that process of decay is random, it's correct to speak about average lifetime τ at some temperature rather than about critical temperature of decay. To determine the temperature dependence of the lifetime of the molecule, τ was calculated as a function of the initial temperature of the system in the temperature range from 300 to 1000 K. Each value of T corresponded to different sets of initial atomic velocities and displacements. The obtained dependence of natural logarithm of lifetime $\ln\tau$ on inverse temperature T^{-1} was approximated by a straight line (Fig. 2). Frequency factor A and activation energy E_a of decay process were derived from the line (see Fig. 2) using the Arrhenius equation.

$$\tau^{-1}\left(T\right) = A\exp\left(-\frac{E_a}{k_b T}\right). \tag{3}$$

For the average values and standard deviations, we obtained $E_a = 0.42 \pm 0.02$ eV and $A = 10^{14.07\pm0.15}\,s^{-1}$. It is worth noting that for the similar calculations for cubane $E_a = 1.9 \pm 0.1$ eV, $A = 10^{16.03\pm0.36}\,s^{-1}$ [12], for hexaprismane $E_a = 0.59 \pm 0.07$ eV, $A = 10^{13.8\pm0.5}\,s^{-1}$ [13] and for octaprismane $E_a = 0.24 \pm 0.04$ eV, $A = 10^{13.1\pm0.6}\,s^{-1}$ [13]. We can see from the plot of the activation energy against the number of vertices of "small" prismanes (Fig. 3) that with increasing of m, the activation energy of the hydrocarbon systems decreases monotonically. So, one can conclude that the kinetic stability of [2, m]prismanes decreases with increasing number of vertices of a closed carbon ring.

4. Conclusions

In the course of this work, we investigated the thermal stability of heptaprismane. Numerical simulation of this dependence was carried out by the nonorthogonal tight-binding model. Based on the obtained results, the temperature dependence of the lifetime of the investigated system was determined. This allowed us to find both the activation energy and the frequency factor of the cluster. Comparison with the results of earlier studies of the cubane, hexaprismane and octaprismane allowed us to make conclusions about the decrease in the thermal stability of "small" prismanes with an increase in the number of vertices of closed carbon rings. Results of this work may be used to provide some insight for new methods of synthesis of carbon heptaprismanes. We expect that obtained data will contribute to further researches of the physical and chemical properties of polyprismanes.

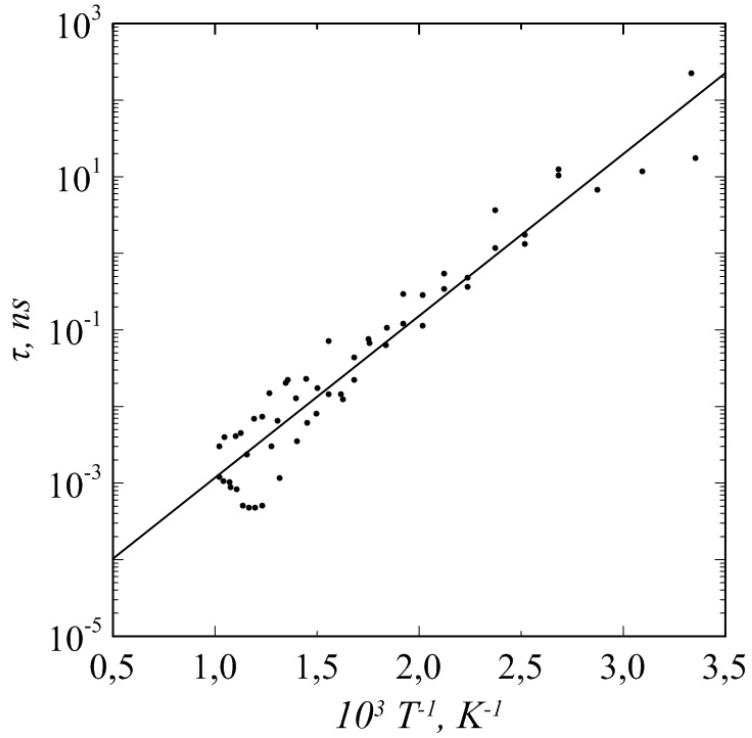

Fig. 2. Dependence of the lifetime τ of heptaprismane on the inverse initial temperature T^{-1}. Circles are calculation results, the solid line is their linear approximation.

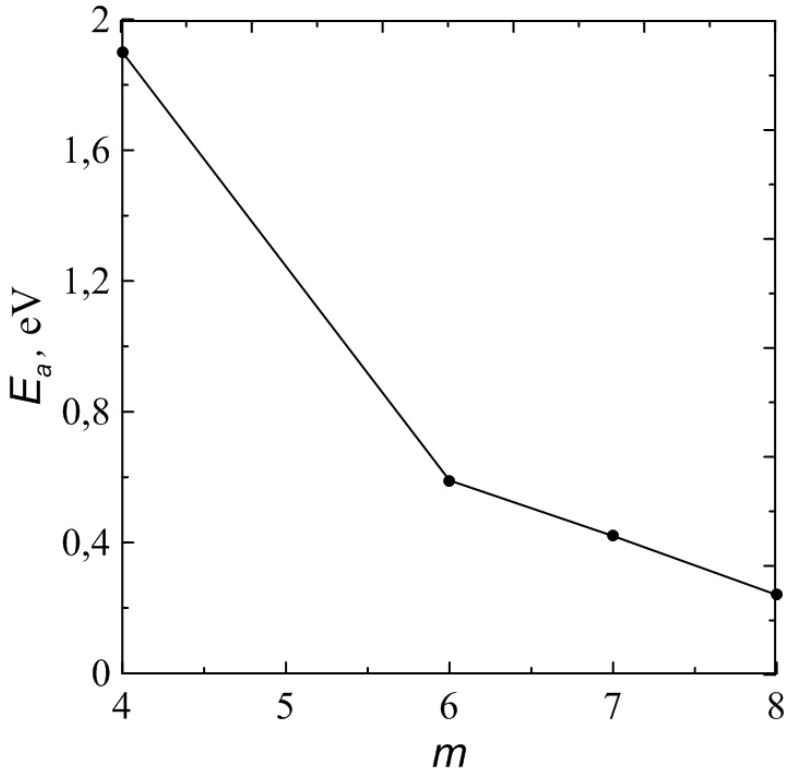

Fig.3. Dependences of the activation energy E_a on the number of vertices m of "small" prismanes. Circles represent calculated data for C_8H_8, $C_{12}H_{12}$, $C_{14}H_{14}$ and $C_{16}H_{16}$ prismanes, respectively.

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