Thermal Stability of C₄₊₄nH₈ Polycubanes

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Abstract — The temperature dependences of the lifetime of polycubanes C₄₊₄nH₈ with n = 2–5 up to their decomposition have been directly calculated using the molecular dynamics method. It has been shown that the activation energy of decomposition of these metastable clusters, in which the C–C bonds form an angle of 90° that is not characteristic of carbon systems, rapidly decreases with an increase in n due to the lowering of the energy barrier that prevents the decomposition of the clusters. This has cast some doubt on the recently made suggestion that there exist nanotubes (n ≫ 1) with a square cross section. Nonetheless, the stability of bicubane (n = 2) and tricubane (n = 3) has proved to be sufficient for their existence at the liquid-nitrogen temperature.

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1. INTRODUCTION

In the best known carbon compounds (diamond, graphene, carbyne), the angles between covalent bonds are equal to 109.5°, 120°, and 180°, which correspond to the sp³, sp², and sp hybridizations of atomic orbitals, respectively (in fullerenes and carbon nanotubes, these angles differ only insignificantly from 120°). Consequently, increased interest has been expressed by researchers both in the C₈H₈ cubane (Fig. 1), which was synthesized for the first time in 1964 [1] and where the angles between all adjacent C–C bonds are equal to 90°, and in the supercubane (Fig. 2) consisting of C₈ “cubes” covalently bound to each other in the directions of their main diagonals (note that, although there are publications on the synthesis of the supercubane, the fact of its existence, as far as we know, has still not been proved [2, 3]). Since so strong “bending” of the C–C–C bonds is energetically unfavorable, the cubane and the supercubane have a substantially strained structure. The cubane structure is stabilized by hydrogen atoms (Fig. 1), whereas the stability of the supercubane is provided by the interaction of neighboring elements C₈ (Fig. 2): in both cases, there is a saturation of “dangling” bonds of the carbon atoms at the vertices of the cube (an isolated cubic cluster C₈ is unstable [4]).

The question now arises as to the possibility of the existence of pure carbon structures that do not contain hydrogen atoms (except, perhaps, for the passivation along the edges) and in which all C–C bonds are either perpendicular or parallel to each other (in the supercubane, this is true only for the C–C bonds within each individual cubic element). In [5], the polycubanes C₄₊₄nH₈ with n = 2–6¹ (Fig. 3) were theoretically investigated using the density functional theory method. It was shown that all their vibrational frequencies are the real quantities; i.e., these hydrocarbon clusters represent metastable (corresponding to local minima of the potential energy) atomic configurations. Later [6], it was noted that, since an increase in n leads to a decrease in the relative number of hydrogen atoms in the polycubane, at n ≫ 1 we are actually dealing with a thinnest carbon nanotube that has a square cross section (hence, here, the term “nanobar” is more appropriate). According to [6], this nanotube can be produced under the deformation of a conventional (2, 2) nanotube.

It should be noted, however, that, although the real values of the frequencies of natural vibrations of the system provide a necessary condition for its metastability, the quantitative characteristic of the degree of stability of the metastable state is the activation energy of its decay Eₐ, which is involved in the Arrhenius formula for the temperature dependence of the lifetime τ of the system in this state; that is,

$$\tau^{-1}(T) = A \exp\left(-\frac{E_a}{k_B T}\right)$$

where A is the frequency factor with dimensionality s⁻¹, T is the temperature, and k_B is the Boltzmann constant. As a rule (even though not always), the value of

¹ For polycubanes, the authors of [5] used the structural formula C₈₊₄nH₈ (n ≥ 1). We believe that the formula C₄₊₄nH₈ (n ≥ 2) is more convenient, because, in this case, n is nothing less than the number of C₈ cubes in the carbon skeleton, which have (at n > 1) common faces, so that n = 1 corresponds to cubane, and n = 2, 3, 4 ..., to bicubane, tricubane, tetracubane, etc.
$E_a$ is close to the height $U$ of the minimum energy barrier separating this metastable state from the configurations with a lower energy. Previously [7], using the molecular dynamics method ("computer experiment"), we directly calculated the dependence of the lifetime $\tau$ on the temperature $T$ for the $C_8H_8$ cubane and demonstrated that the activation energy of its decomposition is $E_a = 1.9 \pm 0.1\text{eV}$. Such a large value of the activation energy $E_a$ indicates a high thermal stability of the cubane and explains why the cubane molecules not only retain their structure at temperatures significantly higher than room temperature [8], but also can form a molecular crystal, i.e., the so-called solid cubane $s$-$C_8H_8$ with a melting temperature of approximately 400 K [9] (during melting of this compound, only the weak van der Waals bonds between the $C_8H_8$ clusters are broken, but the clusters themselves retained their structure).

The main objective of this work is to perform the numerical simulation of the dynamics of polycubanes $C_4+4nH_8$ with $n \geq 2$ over a wide temperature range, as well as to determine the dependences of the activation energies of their decomposition $E_a$ and frequency factors $A$ on the number $n$. We have restricted ourselves to the first four (following the cubane) representatives of the family: bicubane, tricubane, tetracubane, and pentacubane ($n = 2, 3, 4,$ and $5$, respectively). This is enough to make sure that the thermal stability of the polycubanes drastically decreases with increasing $n$. We have also investigated the decomposition of all the aforementioned hydrocarbon clusters, determined the heights $U$ of the energy barriers preventing their decomposition, and demonstrated that, within the limits of error, they coincide with their corresponding values of $E_a$. This paper is organized as follows. Section 2 contains the description of the computational methods. Section 3 presents the results (including the data obtained from the molecular dynamics calculation and static simulation) and their discussion. Section 4 provides the brief conclusion and inferences.

2. COMPUTATIONAL METHODS

The energies of arbitrary atomic configurations were calculated within the framework of the nonorthogonal tight-binding model [10], which represents a reasonable compromise between more rigorous ab initio approaches and extremely simplified classical potentials of the interatomic interactions. This model adequately describes the structural and energy characteristics of various hydrocarbon systems, including both small clusters (cubane [7], methyl cubane [11], etc.), and macroscopic systems (graphane [12], graphyne [13], hydrogen interstitials in diamonds [10], etc.). Yielding to the accuracy of the ab initio methods,