Theoretical modeling of the cubane-based chains, networks and bulks

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Abstract. We have carried out quantum-mechanical calculations of the quasione-dimensional, quasitwo-dimensional and bulk cubane-based structures by means of a nonorthogonal tight-binding potential. The possible existence of these compounds is predicted. Geometries and energetic properties are calculated. We found that the density of supercubane structure is only 2.7 g/cm\(^3\) and it is not a high-density polymorph. The intermolecular bond in such a structure equals to 1.460 Å.

1. Introduction
Cubane C\(_8\)H\(_8\) was first synthesized in 1964 [1]. It is an atomic scale realization of a cube with eight carbon atoms arranged at the corners and single hydrogen atoms bonded to each carbon atom along the body diagonals. The C-C-C bond angle is 90° instead normally sp\(^3\) hybridization angle, which is 109.5°. Cubane forms a molecular crystal at room temperature with relatively high melting point about 400 K [2]. Solid cubane results in a significant amount of strain energy, about 6.5 eV/C\(_8\)H\(_8\) [3]. Because of their high heat of formation, the cubane molecule and its derivatives (for example methylcubane molecule [4]) have been considered to be ideal candidates for novel high-energy materials.

![Figure 1](image1.png)

**Figure 1.** Fragments of the cubane based chains: linear (a), zig-zag (b).
In this paper we report numerical calculations of linear and zig-zag chains (see figure 1), two-dimensional networks (see figure 2) and three-dimensional supercubane structure (see figure 3). All of these structures were built up using different cubane-based clusters (dehydrogenated cubanes) \( C_8H_n \), where \( n = 0, 4, 5, 6, 7 \), as the building blocks, coupled to each other with strong covalent bonds. For example, we use the 1,4-dehydrocubane \( C_8H_6 \) as the elementary fragments for linear chains construction. These materials have been proposed as building blocks for systems with unique novel properties (for example, cubylecubanes – the fragments of one-dimensional chains – have been proposed as building blocks for rigid liquid-crystal compounds [5]). Bulk supercubane structure attracts a special interest. It was first suggested on the basis of an electron diffraction study on a thin film [6]. This structure was called supercubane because it can be described as a bcc arrangement of \( C_8 \) cubes and hence the arrangement of carbon atoms resembles that of cubane \( C_8H_8 \). The supercubane structure was suggested to be a “superdense” polymorph with density greater than density of the diamond.

2. Method of analysis

All calculations were performed using the nonorthogonal tight-binding total energy model [7]. Among the available total energy methods, the approaches from the first principles based on self-consistent electronic structures calculations are highly accurate but they need great costs of the computing resources. On the other hand, the empirical potentials, such as Tersoff-Brenner methods [8] are much faster, but their reliability and transferability are questionable in the unknown phases, because they neglect the electron subsystem. The tight-binding approach is the reasonable compromise between empirical potentials and \textit{ab initio} methods. It describes the materials in a quantum-mechanical manner, while the computational cost is significantly reduced.

Total potential energy of the system \( E_{pot} \) in the tight-binding total energy model can be decomposed into the electronic orbital energy and ionic repulsive energy. The electronic orbital energy is defined as the sum of one-electron energies for the occupied states. Energy spectrum is determined from the stationary Schrödinger equation. 1s orbitals for hydrogen atoms and 2s, 2p\( _x \), 2p\( _y \), 2p\( _z \) orbitals for carbon atoms are considered. This model gives values for intermolecular bonds and binding energies, that agree with the experimental data and \textit{ab initio} results for different clusters and molecules \( C_nH_m \) [7]. Also, this computational technique shows a great accordance with the theory for energy distribution between carbon and hydrogen subsystems for the heat-insulated cubane \( C_8H_8 \) [9].

We use method of structural relaxation for obtaining the equilibrium structures. In the context of this method initial configuration relaxes to the local or global minimum of energy under the influence of intramolecular forces only. The force acting on the atom with index \( k \) is defined as [7]:

\[
F_k = -2 \sum_n \langle \psi_n | \left[ \nabla_k \hat{H} - e_n \nabla_k \hat{S} \right] | \psi_n \rangle - \nabla_k U, 
\]
where $U$ is the classical part of the potential energy, $\hat{H}$ is the tight-binding Hamiltonian, $S$ is the overlap matrix, $|\psi_n\rangle$ and $\varepsilon_n$ are the eigenstates and eigenenergies of the tight-binding Hamiltonian, respectively.

### 3. Geometry and energetics of the investigated cubane-based structures

We analyzed geometries and energetics of different cubane-based structures. The binding energy $E_b$ of linear and zig-zag chains was defined as

$$
E_b = \frac{1}{N_{\text{cluster}}} \left\{ \left( N_{\text{cluster}} - 2 \right) E(C_8H_6) + 2E(C_8H_7) - E_{\text{tot}}(\text{chain}) \right\},
$$

where $N_{\text{cluster}}$ is the number of clusters in the chain, $E_{\text{tot}}(\text{chain})$ is the total energy of the chain, $E(C_8H_6)$ and $E(C_8H_7)$ are the energies of isolated $C_8H_6$ and $C_8H_7$ clusters, respectively. The binding energy $E_b$ of the two-dimensional network was defined as

$$
E_b = \frac{1}{N_{\text{cluster}}} \left\{ 2 \left[ E_1(C_8H_6) + E_2(C_8H_6) \right] + 4 \left( \sqrt{N_{\text{cluster}}} - 2 \right) E(C_8H_4) + \right\} + \left( \sqrt{N_{\text{cluster}}} - 2 \right)^2 E(C_8H_5) - E_{\text{tot}}(\text{network})
$$

where $N_{\text{cluster}}$ is the number of clusters in the network, $E_1(C_8H_6)$ and $E_2(C_8H_6)$ are the energies of isolated isomers $C_8H_6$, differing in positions of H atoms, $E(C_8H_4)$ and $E(C_8H_5)$ are the energies of isolated $C_8H_4$ and $C_8H_5$ clusters, respectively. The maximal investigated network size was 5×5.

**Figure 4.** Binding energies $E_b$ of the linear (circles) and zig-zag (squares) chains versus $1/N_{\text{cluster}}$.

Figure 4 displays binding energies of linear and zig-zag chains $E_b$ as a function of inverse number of clusters $1/N_{\text{cluster}}$ in the structure; $E_b$ depends linearly on $1/N_{\text{cluster}}$. By extrapolation, we obtained the binding energies and intermolecular bond lengths of the macroscopic structures ($N_{\text{cluster}} \gg 1$).

They are 4.58; 4.89; 8.62 eV/cluster and 1.454; 1.458; 1.456 Å for linear chain, zig-zag chain and two-
We also simulated the fragment of bulk supercubane structure. We made hydrogen passivation in order to avoid the interfacial effects. The calculated density of supercubane is only 2.7 g/cm$^3$ (to be compared with $\approx$ 3.6 g/cm$^3$ in diamond). Obtained value is in good agreement with ab initio calculations 2.9 g/cm$^3$ [10]. We found that supercubane is not a "superdense" polymorph. The intermolecular covalent bond in such a structure equals 1.460 Å. Note, that the intramolecular C-C bond in C$_8$ cluster equals 1.600 Å (to be compared with 1.570 Å intramolecular C-C bond in the isolated cubane C$_8$H$_8$ cluster in the context of the same model).

4. Conclusions
Quantum-mechanical simulations of the one-dimensional, two-dimensional and three-dimensional cubane-based structures were carried out by means of the nonorthogonal tight-binding model. The possible existence of these compounds was predicted. Geometries and energetic properties for macroscopic structures ($N_{\text{cluster}} \gg 1$) were calculated. We found that the density of supercubane structure is less than the density of the diamond and it is not a high-density polymorph. It will be interesting to investigate the evolution of these systems under different temperatures, but this problem lies outside the modern development of computational resources. It is necessary to find new methods of analysis of such problems, for example, based on the empirical potentials constructed specially for investigated structures.

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