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# Influence of methyl functional groups on the stability of cubane carbon cage



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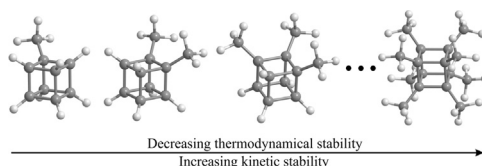
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## HIGHLIGHTS

- Structure, energetics and stability of isolated polymethylcubane molecules  $C_8H_{8-q}(CH_3)_q$  are calculated.
- The mechanisms of isomerization for polymethylcubane family are studied in detail; transition states are identified.
- Single  $CH_3$ -group reduces the stability of carbon cage, but further increasing of radicals makes the framework more stable.
- The estimated lifetime of octamethylcubane at room temperature is about  $\sim 10^9$  s.

## GRAPHICAL ABSTRACT

Polymethylcubanes become less thermodynamically stable as the number of methyl groups attached to carbon cage increases. On the other hand, the increasing of  $CH_3$ -groups makes the carbon framework more kinetically stable.



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## ABSTRACT

We present a quantum-chemical study to elucidate the structure, energetics and stability of isolated polymethylcubane molecules  $C_8H_{8-q}(CH_3)_q$ . The results obtained by means of originally developed nonorthogonal tight-binding approach are in good agreement with the existed experimental data for solid octamethylcubane  $C_8(CH_3)_8$ . The isomerization mechanisms for polymethylcubane family are studied in detail and the minimum energy barriers' heights preventing the decomposition are calculated. The temperature dependence of octamethylcubane molecule lifetime to the decomposition moment was determined by direct molecular dynamics simulation. It is shown that methyl groups destabilize the cubic carbon cage, but less than nitro groups.

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## 1. Introduction

Highly strained cubane-based molecular structures are of both fundamental and applied interest. Cubane  $C_8H_8$ , first synthesized in 1964 [1], belongs to the series of Platonic hydrocarbons. The cage of the cluster is a cube with the vertices occupied by carbon

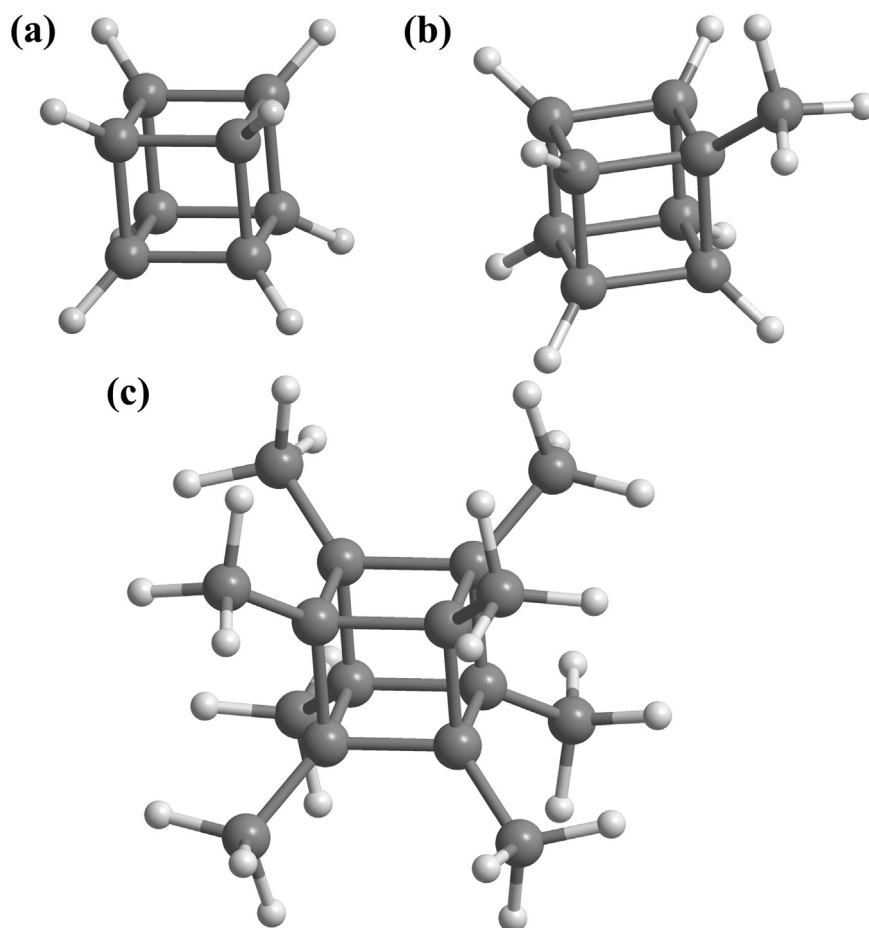


Fig. 1. Molecules of cubane (a), methylcubane (b) and octamethylcubane (c). Dark and light spheres are carbon and hydrogen atoms, respectively.

atoms, so that the angle between the covalent bonds is  $90^\circ$  as distinct from  $sp^3$ -hybridized carbon orbitals with the angle  $109.5^\circ$  (such as a diamond, methane, or ethane). Thus, the angular deformation in the cubane molecule associated with the geometry of the structure is very high [2]. Particular interest in cubane is associated with the possibility of using its derivatives as energetic materials (high-energy-density materials). For example, polynitrocubanes  $C_8H_{8-q}(NO_2)_q$ , cubane derivatives, in which one or more hydrogen atoms are replaced by  $NO_2$  groups, are the promising energy materials [3–5]. Similarly, polymethylcubanes (PMCs), cubane derivatives, in which methyl groups substitute hydrogen atoms (see Fig. 1), are the perspective functional materials as well. For example, methylcubane  $C_9H_{10}$  (Fig. 1b), in which only one hydrogen atom is replaced by the  $CH_3$  group (a liquid under normal conditions), is regarded as a promising nontoxic fuel [6,7].

Both isolated clusters and molecular crystals of polynitrocubanes (see Ref. [5] and references therein) have been extensively studied theoretically and experimentally. Moreover, the most of them (including higher nitrocubanes) were successfully synthesized in laboratory [8,9]. On the contrary PMCs are studied comparatively poor. Only some thermokinetic properties of methylcubane [2,7] and geometry characteristics of molecular solid octamethylcubane [10] were obtained. Furthermore, we could not find any data in the literature concerning the synthesis of isolated  $C_8H_{8-q}(CH_3)_q$  molecules with  $q=2-8$ , but some representatives of polymethylcyclooctatetraene isomers are already obtained [11]. That is why it is interesting to examine how the methyl groups in the molecule influence on the stability of the cubane cage. Earlier we found that nitro groups destabilize the cubic carbon skeleton of

the polynitrocubane compounds due to their effective reciprocal repulsion [12], which makes difficult to synthesize polynitrocubanes with adjacent nitro groups [13]. The role of methyl groups in the cubic cage formation in PMC is not yet clear.

So, the main purpose of this work is to theoretically study the geometric and energetic characteristics of PMCs  $C_8H_{8-q}(CH_3)_q$  with  $q=1-8$ , to determine the mechanisms of their isomerization, to calculate the minimum heights of the energy barriers preventing their decomposition, and to understand the mechanism of methyl groups influence on the carbon cage stability.

## 2. Methods of calculation and computational details

Density functional theory (DFT) with Becke's three-parameter hybrid method and the Lee-Yang-Parr exchange-correlation energy functional (B3LYP) [14,15] with the electron basis set of 6-311 G [16] were used to optimize the geometries and obtain the structural and energy characteristics of the PMCs. The geometries of all PMCs and their isomers were optimized using the GAMESS program package [17].

To obtain the equilibrium structures of the PMCs and the decomposition products we used the method of structural relaxation so that the corresponding initial configuration relaxed to a state with the local or global energy minimum under the influence of intramolecular forces only. For the molecular dynamics simulation of octamethylcubane thermal decomposition and calculation the heights of the energy barriers preventing its isomerization we use nonorthogonal tight-binding total energy model originally developed for H–C–N–O high-energy compounds [12]. The decisive

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