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QUANTUM MECHANICAL INVESTIGATIONS ON STRUCTURE AND STABILITY OF THE SMALLEST DIAMONDOIDS WITH DEFECTS

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Abstract. In this paper we present quantum chemical investigations on structure and stability of the smallest diamondoids with defects. Results of structure, shape and state position in respect each other are also presented. The results of these parameters allow us to found one of the smallest diamondoid particle and foresee what influence to the formation of the particle. Additionally the possible defect places in these particles are investigated and it is showed how electronic structure of the particle is depended on the defect.

1. Introduction

Nanodiamonds have great interest in research over recent decades because they are very promising materials for nanotechnology due to their unique properties which combine mechanical, thermic, radio and chemical stability and large surface area [1-6]. They represent an important class of materials with a great interest in the science of medicine and biology because of ability to be used for drug delivery and bio-labeling applications [7, 8]. For such applications, functionalization of nanodiamonds is needed.

Diamondoids are nanometer-sized, hydrogen-terminated diamond hydrocarbons, i.e. nanodiamonds that are emerging as complementary materials to fullerenes and carbon nanotubes.

Usually the properties of crystalline solids are ordinary investigated without reference of their size when their size is above 10 nm. Only in regime below 10 nm, when the investigated derivatives are recognized as small nanoparticles, the size as well as the shape, number of atoms in the derivatives and so one comes into play because physical as well as chemical properties of the nanoparticles are changed. Two major effects, which are responsible for the size and structure variations in the particles properties, are follows:

1. The number of surface atoms is a large fraction of the total;
2. Intrinsic properties of the interior of particles are transformed by quantum size effects.

The first and simplest member of the diamondoids group, adamantane, is a tricyclic saturated hydrocarbon (tricyclo[3.3.1.1]decane) [9]. The smaller diamondoid molecules are adamantane ($C_{10}H_{16}$), diamantane ($C_{14}H_{20}$), and triamantane ($C_{18}H_{24}$), with the general chemical formula $C_{4n+6}H_{4n+12}$. These lower adamantologues, each has only one isomer. However there is no data found to indicate what smallest size of diamondoids with defect could be.

Although the properties of the particles are their size and shape depended, the particles assume regular shape, with the same well-defined faces as are present in extended crystals [10]. Hence, we predict that the particles, possessed some properties of the crystalline solids, must contain just enough atoms to have identifiable interior.

It is well known that diamond cubic is in the Fd3m space group, which follows the face-centered cubic bravais lattice. The lattice describes the repeat pattern. For diamond cubic crystals this lattice is "decorated" with a motif of two tetrahedrally bonded atoms in each primitive cell, separated by 1/4 of the width of the unit cell in each dimension [11]. The number of atoms in the lattice is 18. Thus we intend investigate nanoparticles consist of the 18 carbon atoms which arrangement describes face-centered cubic bravais lattice. Here, it is of considerable interest to understand solid-solid phase transition in two cases: small carbon particles are coated by hydrogen; the diamondoid possess defects, because the derivatives may prove one of the most diverse and powerful ideals for a "quantum dots". It is noted, that only the highest symmetry cases are investigated here.

2. Description of method

The stabilities and the electronic structure of the small nanodiamonds were investigated by using the generalized gradient approximation for the exchange-correlation potential in the density functional theory (DFT) as described by Becke’s three-parameter hybrid functional, using the non-local correlation and provided by Lee, Yang, and Parr. The DFT method is commonly referred to as B3LYP [12, 13] - a representative standard DFT method. The TZV basis set for C, N and H atoms has also been used [14]. The structures of the investigated nanoparticles have been optimized globally without any symmetry constraint and by starting from initial geometries that correspond to the structure of the nanodiamond cell. Hence, the initial geometry of clusters was constructed according to a certain symmetry, why the defect (N atom) place was change. Thus, in our case five different structures were investigated. The set of starting configurations was extensive enough due to high symmetry of the investigated diamondoids. The GAMESS program suite was used for all simulations here [15].

3. Results and discusion

Let us remember that, there is an infinite number of possible surfaces which can be exposed for every crystal system. In practice, only a limited number of planes are found to exist in any significant amount. Thus, the attention was concentrated on the above surfaces, because it is possible to predict the ideal atomic arrangement for a given surface of a particular metal by considering how the bulk structure is intersected by the surface. The crystalline structure that is expected to be in the investigated nanoparticles was obtained on the basis of the symmetry of a bond and atom location in the planes. Let us remember that face-centered-cubic lattice is cubic in shape with identical atoms at each corner and in the center of each face. Moreover, the more covalent materials tend natural to assume tetrahedral shapes characteristics of the diamond. The tetrahedrally bonded atoms can be viewed along any of three axes as sheet of hexagonally shaped chair structures. It implies, that in the nanodiamond consist of 18 C atoms, at least four atoms are not joined with others carbon atoms and their position in the particle could be related with H atoms number. Thus we are firstly investigated nanodiamonds consist of 18 C atoms surrounded by different number of H atoms: 32 and 28 to find non-mentioned small diamondoids. The number of H atoms is chosen in respect of a number of possible C-C and C-H bonds. Obtained results indicated, that in the case of larger number of H, the two C atoms (that were in the corner of cube) are joined with the H atoms that leads to formation of two CH_4 molecules, while other two corner C atoms joined with symmetrically placement C atoms at the face of the cube and three H ones (Fig. 1). To be sure that the CH_4 molecules do not influence to stability of the nanodiamond, the obtained structure was recalculated. The structure is called I to simplify communications.

In the case of particle consist of 18 C atoms surrounded by H atoms that number is insufficient to form the CH_4 molecules and cover all particle surface, we received that all cube-corner C atoms could joined with symmetrical face centered C atoms and 3 H atoms (Fig. 2). The structure is below called II. It is interesting, that results of our investigations indicate that between the smaller diamondoid molecules the $C_{16}H_{28}$ should be mentioned too.

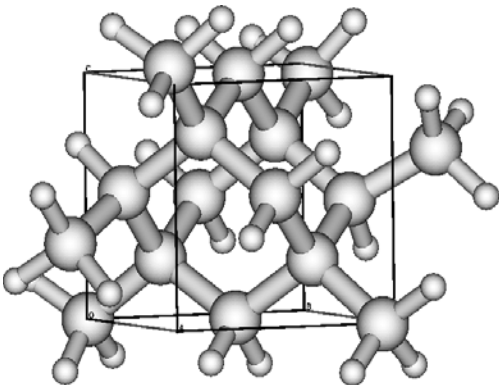

Fig. 1. The structure of the investigated nanodiamond consists of 16 C atoms and 28 H atoms located in the cubic cell. The structure is called as I.

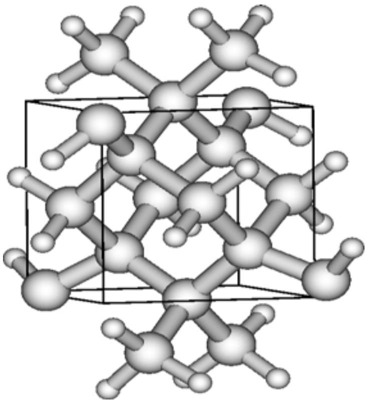

Fig. 2. The structure of the investigated nanodiamond consists of 18 C atoms and 24 H atoms located in the cubic cell.The structure is called as II.

In the above cases, the structures of these particles remain face-centered-cubic with similar lattice parameters 3.54 and 3.60 Å of structure I and II respectively. The three surfaces are obtained in the above structures too. Both obtained structures are stable (Table 1). More interesting is that the energy formation per atom of the above structures is approximately equal while the HOMO-LUMO gaps, indicated chemical stability (possibility to make new chemical bonds), are very different. The gap of structure I is approximately twice larger than those of structure II. It allows us to speculate that there are some critical number of carbon atoms and carbon/hydrogen atom rate, when the nanodiamonds are chemically stable. Moreover, it indicates that the obtained structure that is not mentioned between the smallest diamondoids is more stable than triamantane. On the other hand, the results obtained indicate that the nanodiamonds may be smaller than the described particles and the smallest particle could be more stable than our investigated.

Based on the obtained results, we predict that nanodiamond defect (nitrogen atom appearance instead carbon atom) could appeared in the structure I simpler than in structure II because of the lower chemical stability. Hence, we investigated stability and structure of the nanodiamonds in which position of nitrogen atom is different (Figs. 3-6). The number of hydrogen atoms in investigated particles was change in accordance of the position of nitrogen atoms, i.e. when the nitrogen atom is in the corner of the cube lattice, then the total number of hydrogen atoms in the particle is less by one than in the initial structure of the nanodiamond without defects. This variation is related with chemical properties of the nitrogen atom: usually only three atoms could share their electrons with the nitrogen atoms. That way the nitrogen has a filled outer shell and only two hydrogen atoms have two electrons to fill their shells when C-N bond is formed.

Table 1. Energy formation and HOMO-LUMO gap of the structures investigated.

Compound	**Energy formation, eV**	**Energy formation per atom, eV**	**HOMO-LUMO gap, eV**
Structure I	213.54	4.85	6.49
Structure II	202.67	4.83	2.80
Structure III	167.60	4.93	2.13
Structure IV	197.8376	4.82	1.97
Structure V	164.26	4.83	1.82
Structure VII	198.18	4.83	2.01

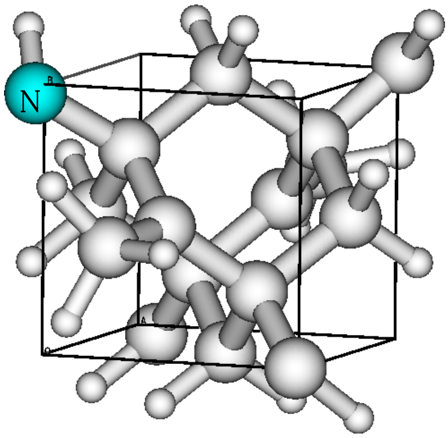

Fig. 3. The structure of the investigated nanodiamond consists of 15 C atoms N and 18 H atoms located in the cubic cell. The structure is called as III.

According to results obtained, in two structures from four investigated, two CH_3 molecules should be formed. The molecules are formed by the carbon atoms that are in the corner of the cube lattice, while other corner-carbon atoms are joined with three H atoms and face-centered-carbons (Figs. 3-5). These two structures were recalculated to be sure that the CH_3 molecules do not influence to stability of the nanodiamond.

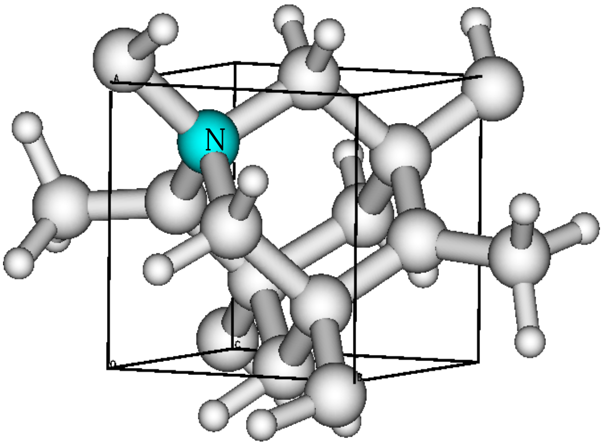

Fig. 4. The structure of the investigated nanodiamond consists of 15 C atoms, N and 18 H atoms located in the cubic cell. The structure is called as V.

Firstly, it is necessary to mention that the main structure of the diamondoids is obtained in all our investigated particles with defects. The structural difference between these particles and diamondoids are following:

1. The corner-cube-carbon atoms should be out of the cube plane;
2. In several cases the number of the carbon atoms is insufficient to form center-cube lattice, but tetrahedral shape characteristics of the diamond are assumed.

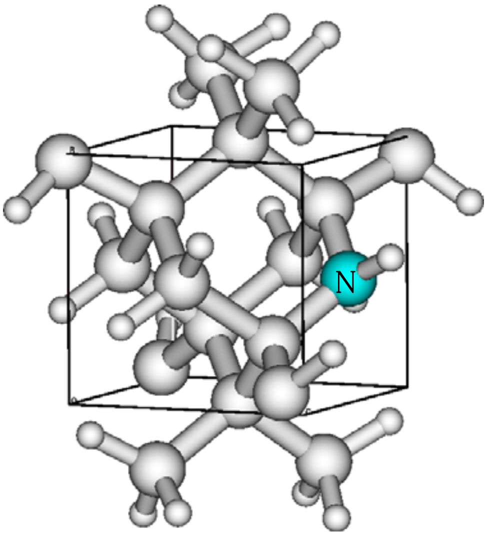

Fig. 5. The structure of the investigated nanodiamond consists of 17 C atoms, N and 23 H atoms located in the cubic cell. The structure is called as II.

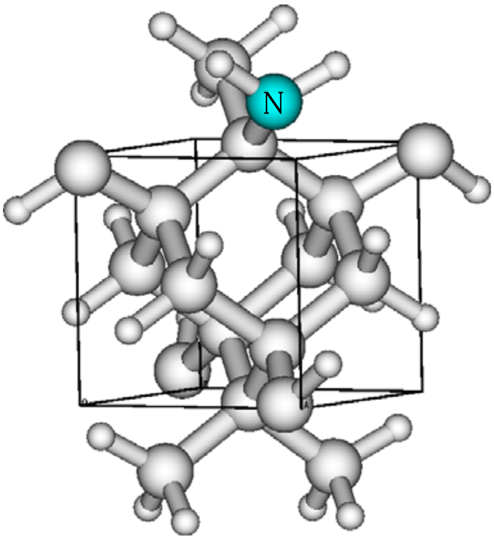

Fig. 6. The structure of the investigated nanodiamond consists of 17 C atoms, N and 23 H atoms located in the cubic cell. The structure is called as VI.

Moreover, the lattice parameters of the particle are not defect position depended and coincides with that of the above described diamond particle (Table 2).

Table 2. Lattice parameters of the structures investigated.

Particle	**Structure III**	**Structure IV**	**Structure V**	**Structure VII**
Lattice parameter, Å	3.51	3.60	3.52	3.55

The stability of the particles investigated are not defect position depended too as chemical stability (Table 1). It is necessary to note, that Structure III and Structure V are open shell system, however it is not possible to foresee tendency to form new chemical bonds based on the result of investigations of HOMO-LUMO gap and the particle energy of formation. Moreover, we checked what happens when the structures becomes closed or open shell system in the case where it is possible, i.e. H atoms is joined with N in Structure III and one N-H bond disappeared in the Structure VII. It is interesting, that the additional H atom adding to the initial geometry of the structure III, the equilibrium geometry of these systems is different. In the cases the H adding (Structure III a) CH_3 or CH_4 molecules are not formed and shape of the particle looks like shape of the particles IV and VII (Fig. 8).

However, when one N-H bond disappeared, results of investigations prove that one CH_3 molecule should formed and structure of the particle is some mixture of the structures of the described diamondoids (Fig. 9).

The particles possess also face-centered-cube structure with lattice parameter 3.55 Å that fits results presented above. The energy of formation per atoms of the particle is 4.85 eV and 4.95 eV for modified Structure III and Structure VII respectively and it coincides also with that of other described particles. Of course, the HOMO-LUMO gap becomes larger (2.62 eV and 2.70 eV) than that of the particle with open shells, hence, the particle has less possibility to form new chemical bonds.

It is very well known, that a semiconductor must have at least two characteristics:

1. the bonding and anti-bonding orbitals must form a delocalized band;
2. the HOMO-LUMO gap in molecular species should be generally of the order of 0.5 eV to 3.5 eV.

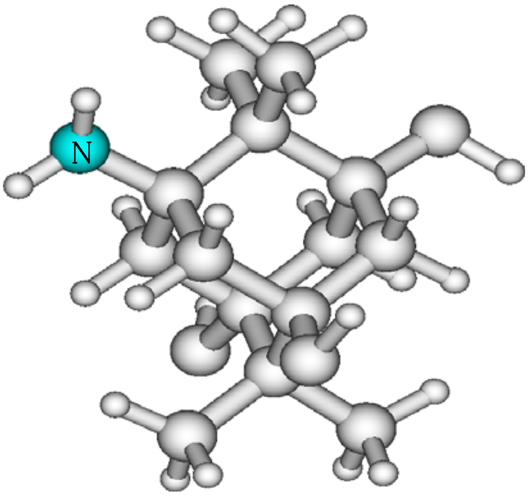

Fig. 7. View of the structure that is received when an additional H atom is added to the structure III. The structure of the investigated nanodiamond consists of 17 C atoms, N and 25 H atoms. The structure is called VII.

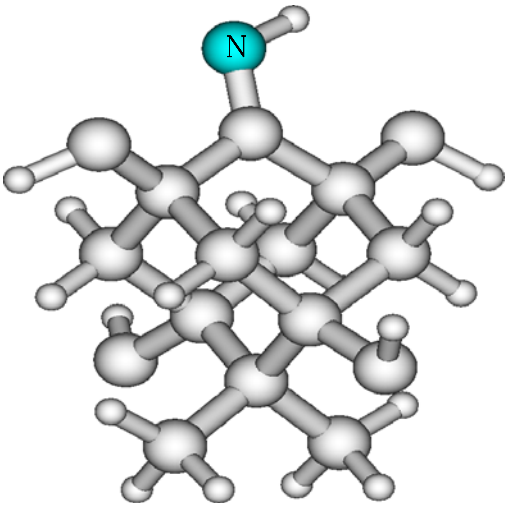

Fig. 8. View of the structure that is received when one H atom is removed from the structure VII. The structure of the investigated nanodiamond consists of 16 C atoms, N and 19 H atoms located in the cubic cell.
The structure is called VIII.

HOMO-LUMO gaps of the investigated derivatives belong to the above range, but the orbitals of the investigated structures form localized band. The above results prove investigations of the states (Fig. 9). It is possible to see that states are widely enough scattered in energy, they are too far (more than 0.04 eV) apart to overlap much with each other. Thus, an electron in one such state must change its energy in order to move. Based on the results we may speculate that investigated diamondoids do not possess semiconductor properties.

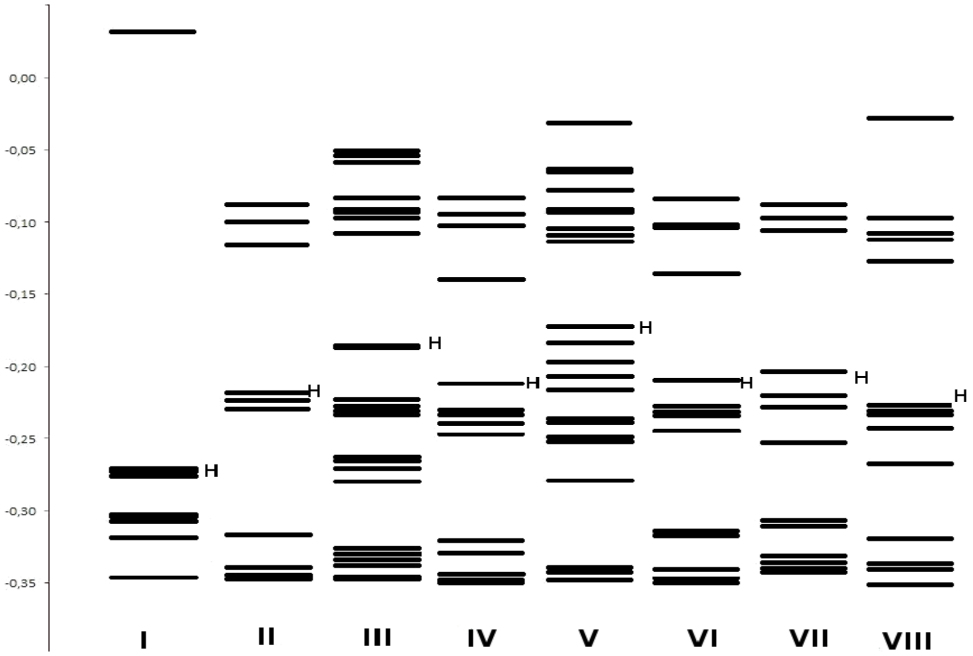

Fig. 9. Displacement of state of the investigated structures. H letter indicate the Highest occupied state. The structures III and V are open shell system, thus one-electron states are presented in the case while two-electron states are presented in rest cases. It should be noted to evaluate the state are widely enough scattering is investigated.

4. Conclusions

Quantum chemical investigations on structure and stability of the smallest diamondoids with defects are performed. It is necessary to mention that the simulation results allow us speculate that the diamondoid (without and with defect) size as well as shape is H atom number depended, i.e. naturally the large hydrogen atom number leads to the formation of the cluster resembling CH_4 molecules, while the above molecules tend to form C-C bond with nano-diamonds cage when the H number is smaller.

We found that between the smaller diamondoid molecules the $C_{16}H_{28}$ should be mentioned too: the particle stability is similar well known diamondoid such as triamantane.

The structure of our investigated particles remains face-centered- cubic with similar lattice parameter 3.54 -3.60 Å. However, despite the similarity of the geometrical structure, the chemical stability (possibility to make new chemical bonds) of the investigated particles are very different. It allows us to speculate that there is some critical number of carbon atoms and carbon/hydrogen atom rate, when the nanodiamonds are chemically stable.

It is necessary to mention that the main structure of the diamondoids is obtained in all our investigated particles with defects. The structural difference between the diamondoids with defect and diamondoids are following:

1. The corner-cube- carbon atoms should be out of the cube plane;
2. In several cases the number of the carbon atoms is insufficient to form center-cube lattice, but tetrahedral shape characteristics of the diamond are assumed.

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