

Stone-Wales defects in nitrogen-doped C₂₀ fullerenes: Insight from *ab initio* calculations



Konstantin P. Katin^{a,b,*}, Mikhail M. Maslov^{a,b}

^a Department of Condensed Matter Physics, National Research Nuclear University “MEPhI”, Kashirskoe Shosse 31, Moscow 115409, Russia

^b Laboratory of Computational Design of Nanostructures, Nanodevices and Nanotechnologies, Research Institute for the Development of Scientific and Educational Potential of Youth, Aviatorov Street 14/55, Moscow 119620, Russia

ARTICLE INFO

Keywords:

Kinetic stability

Transition state

DFT

C₁₉N

C₁₈N₂

C₁₇N₃

ABSTRACT

Density functional theory is applied to study the mechanism of the Stone-Wales defect formation in unsubstituted and nitrogen-doped dodecahedral C₂₀ fullerenes. We obtained the molecular structures of ideal and defected cages as well as the transition states separating them. Depending on the number of nitrogen atoms and their relative position on the cage surface, Stone-Wales defect is formed through the single additional intermediate state or directly. The activation energy barrier of the defect formation reduces from 4.93 eV in pure C₂₀ to 2.98 eV in single-doped C₁₉N, and reaches ~ 2 eV under further doping. All considered nitrogen-doped fullerenes possess high kinetic stability at room temperature. However, they become much less stable at temperatures of about 750 K that are typical for the fullerene annealing process.

1. Introduction

Nitrogen doping of carbon fullerenes provides the possibility for the modification of their reactivity and electronic properties [1,2]. It should be noted that typical C–C bond lengths in fullerenes are close to the C–N distance in trimethylamine, which is equal to 1.451 Å [3]. Thus, the nitrogen atoms can replace the carbon atoms in a fullerene cage without perceptible structural deformations of the latter. Nitrogen substituents provide *n*-doping of fullerenes and therefore significantly change their electronic characteristics. So, the nitrogen-doped fullerenes are the promising candidates for the active parts of nanoelectronic devices [1], as the cathode catalysts for hydrogen fuel cells [4], or as the adsorbents for Tabun nerve agent [5].

The first nitrogen substituted derivatives of C₆₀ and C₇₀ were synthesized in 1991 *via* the contact-arc vaporization of graphite in a partial atmosphere of gaseous N₂ and NH₃ [6]. Then, a series of N-doped [60]fullerenes were isolated as well, including C₅₉N [7], C₅₇N₃ [8], and C₄₈N₁₂ [9]. Successful synthesis of N-substituted fullerenes stimulated their further theoretical studies: energy, geometrical and electronic properties were calculated for the C₁₉N [10], C_{20–*n*}N_{*n*} (*n* = 1–12) [11], C₃₄N₂ [12], and C_{60–*n*}N_{*n*} (*n* = 1–12) [13] molecules. Significant charge transfer between the carbon and nitrogen atoms was detected for both C_{20–*n*}N_{*n*} (*n* = 1–12) [11] and C_{60–*n*}N_{*n*} (*n* = 1–12) [13] molecular systems. Note that all these N-doped fullerenes turned out to be true minima on the corresponding potential energy surfaces (PES).

Nevertheless, replacement of carbon atoms by nitrogen atoms in a highly strained carbon cage can induce the defect formation at non-zero temperatures. For example, nitrogen doping reduces the activation energy barrier for Stone-Wales defect [14] formation by 2.28 eV [15] in (6,6) single-walled carbon nanotube. Thus, one can expect the similar or even greater reduction of isomerization energy barriers for more curved surfaces of N-doped fullerenes.

The smallest fullerene C₂₀ is less kinetically stable than the higher fullerenes such as C₃₆ or C₆₀ [16,17], due to its stronger curvature. Nevertheless, the lifetime of the C₂₀ cage at room temperature is found to be very large (practically, “infinite”) [18]. The defect formation in unsubstituted C₂₀ were previously studied both in the frame of semiempirical molecular dynamics simulations [18,19] and *ab initio* calculations of corresponding potential energy surfaces [16]. However, substitution of carbon atoms by the nitrogen atoms in the fullerene cage can accelerate the defects formation. Despite the intensive studies of C_{20–*n*}N_{*n*} systems [10,11] and the prospects of their application [4], kinetic stability and defect formation processes in these metastable compounds have not yet been studied. At the same time, structural defects can significantly change their energy and electronic characteristics as well as kinetic stability. It was shown for the Stone-Wales defects in fullerene C₃₆ [20], non-classical fullerene C₄₆ [21], nitrogen-doped carbon nanotubes [22], graphene [23] and graphene nanoribbons [24].

In this paper, we present a theoretical study of defects formation in

* Corresponding author at: Department of Condensed Matter Physics, National Research Nuclear University “MEPhI”, Kashirskoe Shosse 31, Moscow 115409, Russia.
E-mail address: KPKatin@yandex.ru (K.P. Katin).

unsubstituted and nitrogen-doped $C_{20-n}N_n$ ($n = 0-3$) fullerenes. The effect of one, two and three doping nitrogen atoms on activation energy barrier that should be overcome for dodecahedral cage conversion into its defective isomer is investigated in detail.

2. Computational details

Our calculations are performed in the frame of density functional theory. Since we consider molecular systems with a multiplicity different from unity, restricted open-shell formalism is applied. The B3LYP hybrid exchange-corrected functional [25,26] with the 6-311 G(d,p) electronic basis set [27] is used. For C_{20} isomerization process we obtain the minimum energy path (MEP) using the nudged elastic band (NEB) method [28] as it is implemented in the TeraChem program package [29–32]. We use the Newton-Raphson method for the local minima and transition states finding. Optimization procedures are continued until the residual forces acting on atoms become lower than 10^{-4} Ha/bohr. For all located stationary points the hessian matrix is calculated at the same level of theory and the frequency analysis is performed for confirming the true minima (there are no imaginary frequencies in the spectrum) or transition states (frequency spectrum contains only one imaginary frequency). Next, the intrinsic reaction coordinate analysis is performed to confirm that the located transition states separate the corresponding minima. All calculations excluding NEB are carried out using the GAMESS software [33].

3. Results and discussion

First of the all, the geometries of unsubstituted C_{20} fullerene and its nitrogen-doped derivatives were optimized (see Fig. 1). Note that there are five various dodecahedral $C_{18}N_2$ isomers. Their molecular structures are presented at Fig. 1c. Their relative energies are (in eV) 0 (reference point), 0.05, 0.08, 0.29, and 0.44 for $C_{19}N_2$ -(1), $C_{19}N_2$ -(2), $C_{19}N_2$ -(3), $C_{19}N_2$ -(4), and $C_{19}N_2$ -(5) isomers, respectively. It is found that the $C_{19}N_2$ -(4) and $C_{19}N_2$ -(5) isomers with the closest relative position of nitrogen atoms on the cage surface are the most energetically unfavorable. Probably, the Coulomb repulsion between the neighboring nitrogen atoms leads to the destabilization of the fullerene cage. Detailed Lowdin population analysis shows that nitrogen atoms in fullerene cage are positively charged (see Table 1). Note that the analogous effect was previously observed for the N-doped graphene [34].

In addition, nitrogen atoms change the electronic characteristics, namely HOMO-LUMO gap, of fullerene cage (see Table 1). Every subsequent nitrogen replacing the carbon in the cage significantly changes HOMO-LUMO gap of the system. It can be said that the HOMO-LUMO gap shows the oscillatory behavior depending on the number of substituting nitrogen atoms in the cage.

Thus, we further consider more energetically favorable $C_{18}N_2$ isomers (labeled as $C_{18}N_2$ -(1), $C_{18}N_2$ -(2), and $C_{18}N_2$ -(3) at Fig. 1c), and $C_{17}N_3$ isomer with the maximally separated nitrogen atoms on its cage surface (Fig. 1d). Frequency analysis confirms that all these structures are the true minima on the PES. Thermochemical data calculated for the normal conditions and for the temperature $T = 750$ K that is typical for the annealing of nitrogen-doped fullerenes [8] are listed in the Table 2. It contains energies ΔE , enthalpies ΔH , and Gibbs energies ΔG for the reactions of the form $\frac{20-n}{20}C_{20} + \frac{n}{2}N_2 \rightarrow C_{20-n}N_n$, where n is the number of substituting nitrogen atoms. Electronic, vibrational, translational, and rotational contributions to the thermodynamic potentials are taken into account, the approximation of the ideal gas is used.

Kinetic stability of the fullerene cage is associated with the possible defects that can appear on its surface at non-zero temperatures. According to the previous *ab initio* studies the Stone-Wales defect has the lowest activation energy barrier among all defects possible in

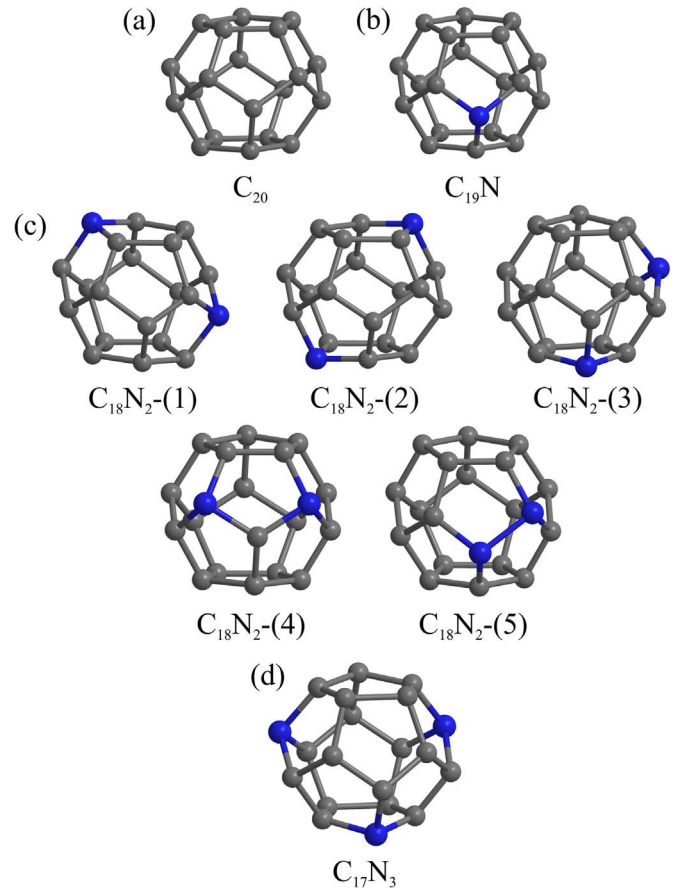


Fig. 1. Molecular structures of (a) C_{20} , (b) $C_{19}N$, (c) $C_{18}N_2$, and (d) $C_{17}N_3$ cages. Grey and blue colors denote the carbon and nitrogen atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 1

Lowdin charge on nitrogen atoms and HOMO-LUMO gap for the $C_{20-n}N_n$ ($n = 0-3$) fullerenes studied.

Fullerene	Lowdin charge on nitrogen atoms, $ e /\text{atom}$	HOMO-LUMO gap, eV
C_{20}	–	1.93
$C_{19}N$	0.067	0.88
$C_{18}N_2$ -(1)	0.075	2.40
$C_{18}N_2$ -(2)	0.088	2.01
$C_{18}N_2$ -(3)	0.073	2.09
$C_{18}N_2$ -(4)	0.064	2.15
$C_{18}N_2$ -(5)	0.044	2.22
$C_{17}N_3$	0.084	0.65

Table 2

Energies ΔE (kJ/mol), enthalpies ΔH (kJ/mol), and Gibbs energies ΔG (kJ/mol) of the reactions of the form $\frac{20-n}{20}C_{20} + \frac{n}{2}N_2 \rightarrow C_{20-n}N_n$. Pressure is equal to standard value (101.3 kPa).

System	n	$T = 298$ K			$T = 750$ K		
		ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
C_{20}	0	0	0	0	0	0	0
$C_{19}N$	1	3319.7	3318.6	3343.0	3322.3	3319.5	3379.9
$C_{18}N_2$ -(1)	2	5927.4	5925.2	5976.5	5929.5	5924.0	6056.2
$C_{18}N_2$ -(2)	2	6070.9	6068.6	6118.0	6073.7	6068.1	6194.1
$C_{18}N_2$ -(3)	2	6134.9	6132.5	6183.6	6137.1	6131.6	6262.9
$C_{17}N_3$	3	9971.0	9967.6	10038.9	9976.4	9968.1	10148.5

Download English Version:

<https://daneshyari.com/en/article/5449944>

Download Persian Version:

<https://daneshyari.com/article/5449944>

[Daneshyari.com](https://daneshyari.com)