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DFT Investigation of CH_2O Adsorption on Pristine and Doped Graphene

Mohsin M. Meteab and Abbas H. Abo Nasriya
Department of Physics, Faculty of Science, University of Kufa, Najaf, Iraq

Abstract: The sensitivity of Pristine Graphene (PG), Boron-doped graphen (B-doped graphene), Nitrogen-doped graphene (N-doped graphene) and Sluminum-doped graphene (Al-doped graphene) for one atom toward gas molecule CH_2O by using Gaussian 09 program which applies the Density Functional Theory (DFT) with (P_3 LPY) functional and 6-31G basis set. The results show that the adsorptions of CH_2O on B-doped graphene (on atom and center ring) are weak physisorption with an adsorption Energy (E_{ad}) (0.273) (0.315) $_{\text{center ring}}$) eV, otherwise doped graphene for this atom could be a good sensor for this gas CH_2O. For except the adsorption of CH_2O on PG, N-doped graphene and Al-doped graphene on the (atom and center ring) are a strong chemisorption in this case, could catalyst or activate, suggesting the possibility of as a metal-free catalyst.

Key words: Graphene, gas adsorption, density functional theory, HOMO and LUMO, adsorption, metal

INTRODUCTION

A great interest has recently been given to the field of carbon nanotubes. In this regards, many researches have been conducted considering the carbon nanotubes, graphene and fullerenes. The potential applications of these materials are important. Among miscellaneous nanostructures, fullerenes are known as suitable option for drug delivery due their appropriate properties which include hydrophobic characteristic, unique spherical structure, efficient drug loading together with their few side effects in biological media (Latif and Dickert, 2015; Muhammad *et al*., 2017). So far, experimental and theoretical studies have been carried out on C60 (Muhammad *et al*., 2017; Nasriya, 2018). The aforementioned drug nano-carrier is potentially appropriate to promote the therapeutic efficiency of drug, since it can be engineered to moderate the release and the stability of drug in order to prolong the spread time of drug, protecting it from elimination by phagocytic cells or premature degradation.

Despite the notable advantages of experimental researches, the empirical methods are expensive and time consuming. For this, the application of computational methods has been increasingly extended (Rad and Foukolaei, 2015).

MATERIALS AND METHODS

Computational details of DFT: In this research, fully optimized geometries has been done at the B3LYP/6-31G* level of theory as implemented using suitable Version of Gaussian 09. This software package is using the standard and modern quantum mechanics basics (Mohmmed, 2017; Nasriya, 2018). We calculate the chemical potential or Fermi Energy (E_F) of the complexes as given:

$$E_F = E_{HOME} + E_{LUMO}/2 \quad (1)$$

Where:

E_{HOMO} = The Energy of the Highest Occupied Molecular Orbital

E_{LUMO} = The Energy of the Lowest Unoccupied Molecular Orbital

The energy gap in Energy levels (E_g) of a system is defined as:

$$E_g = E_{LUMO} - E_{HOME} \quad (2)$$

The adsorption Energy (E_{ads}) was evaluated using the following approximate expression:

$$E_{ads} = E_{COMPLEX} - (E(molecule) + E_{gas}) \quad (3)$$

Where:

$E_{COMPLEX}$ = The total energy of the molecule with adsorption with gas

$E_{(molecule)}$ = The total energy of the studied molecule without adsorbed

E_{gas} = The total energy of the gas molecule (Glendening *et al*., 2001)

RESULTS AND DISCUSSION

After relaxation of CH_2O adsorbed on PG, B-doped, N-doped graphene and Al-doped graphene is shown in Fig. 1. Meanwhile, the bond lengt hs of C-C, C-N, C-B and

Corresponding Author: Abbas H. Abo Nasriya, Department of Physics, Faculty of Science, University of Kufa, Najaf, Iraq

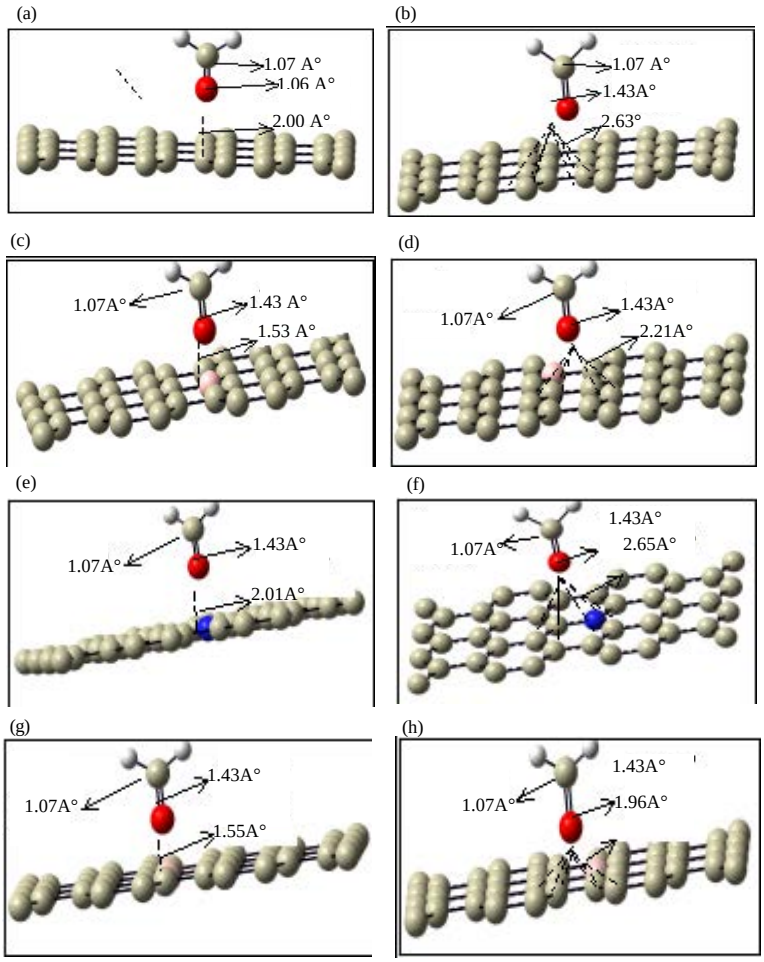

Fig. 1: Initial structures of the studied complexes with CH_2O gas; a) C_{42}-C-H_2-O; b) C_{42}-C-H_2-O center; c) C_{41}B-C-H_2-O; d) C_{41}B-C-H_2-O center; e) C_{41}N-CH_2-O; f) C_{41}N-CH_2-O center; g) C_{41}Al-CH_2-O and h) C_{41}Al-CH_2-O

Table 1: Structural and electronic properties of adsorption of CH_2O molecules on PG, B-doped graphene, N-doped graphene and Al-doped grapheme

Property Ev	a	b_{center}	c	d_{center}	e	f_{center}	g	h_{center}
E_{tot}	-46622.974	-46622.960	-46272.340	-46272.298	-47088.347	-46622.960	-52124.876	-52124.610
E_{ads}	12.587	12.600	0.273	0.315	15.917	14.014	1.261	1.527
E_g	2.345	2.340	0.252	0.758	1.868	2.330	0.048	0.042
IP (=-EHOMO)	6.337	6.347	3.171	5.877	6.089	6.347	5.027	4.961
EA (=-ELUMO)	3.992	3.999	2.919	5.119	4.220	3.999	4.978	4.919
E_F	-5.164	-5.173	-3.045	-5.538	-5.154	-5.173	-5.002	- 4.940

C-Al are 1.438, 1.529, 1.414 and 1.844 Å, respectively are consistent with the other results (Ma *et al*., 1998) which basically decrease and increase of electrons decrease and increase in the elements (Dai and Yuan, 2010). From Fig. 1a, the side view of gas molecules CH_2 O adsorb.

C-atom of PG on the distance (2.0 Å), the Fig. 1b shows that the gas CH_2O on the center ring of PG with (2.63 Å) the CH_2O of the doped atom (B-doped PG) on the distance (1.57 Å) it note that on the Fig. 1c and d gas molecular on the center ring B-doped PG on the distance (2.21 Å), the CH_2 O of the doped atom (N-doped PG) on the distance (2.01A) is observed that on the Fig. e and f) gas molecular on the center ring N-doped PG for the distance (2.65 Å) the CH_2 O of the doped atom (Al-doped PG) for the distance (1.55 Å) we see that on the Fig. 1g and h gas molecular on the center ring Al-doped PG on the distance (1.96 Å) (Fig. 2).

It can be noticed from Table 1 that E_{Tot} for adsorption of CH_2O on N-doped graphene and Al-doped grapheme and (adsorption center) are larger than adsorbed PG, this indicates that E_{Tot} increases (in magnitude) with increasing the number of atoms while the E_{Tot} for adsorption of CH_2O on B-doped grapheme are smaller than adsorbed PG because that decreases (in magnitude) with decreasing the number of atoms. And adsorption Energy (E_{ad}) of

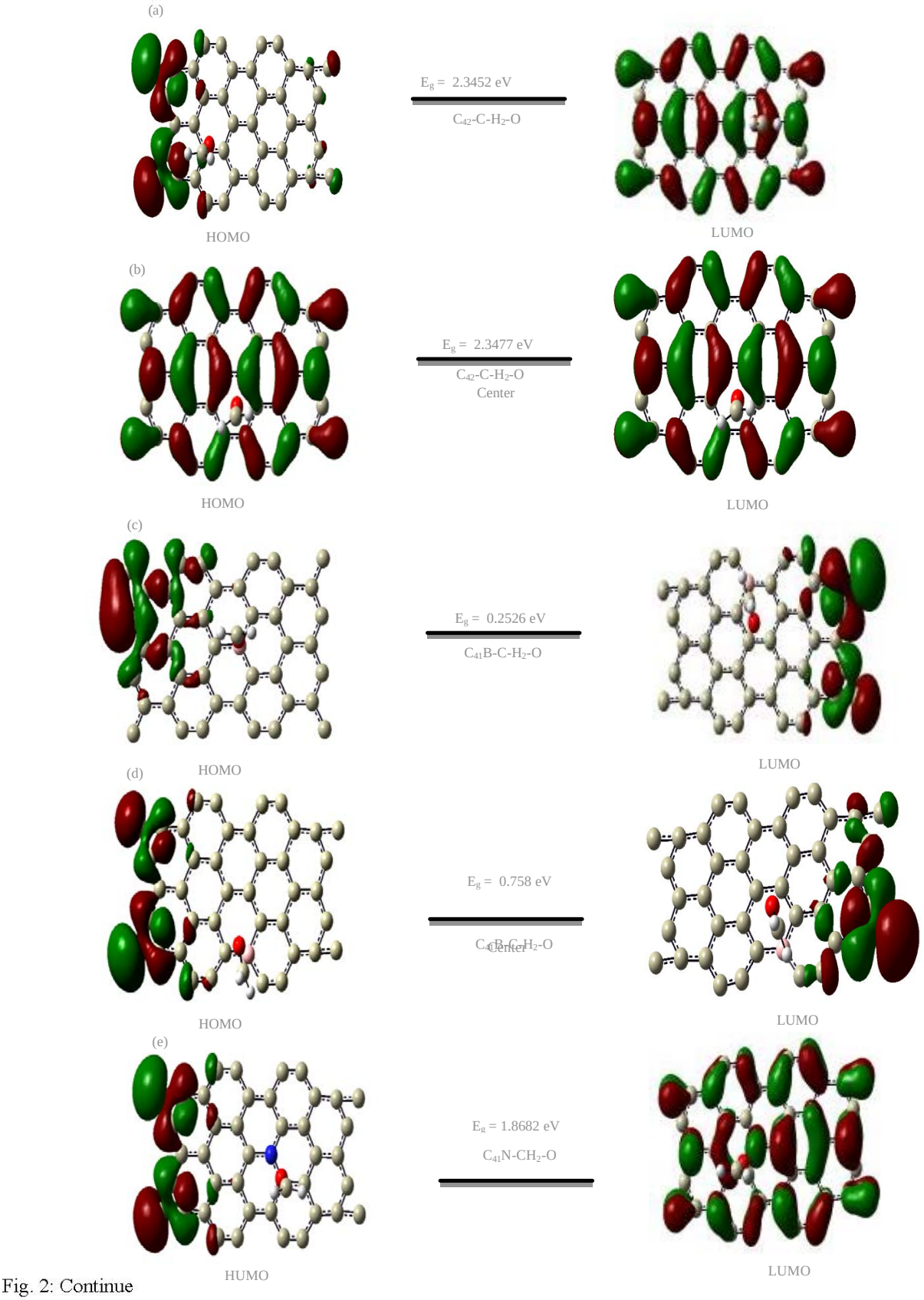

Fig. 2: Continue

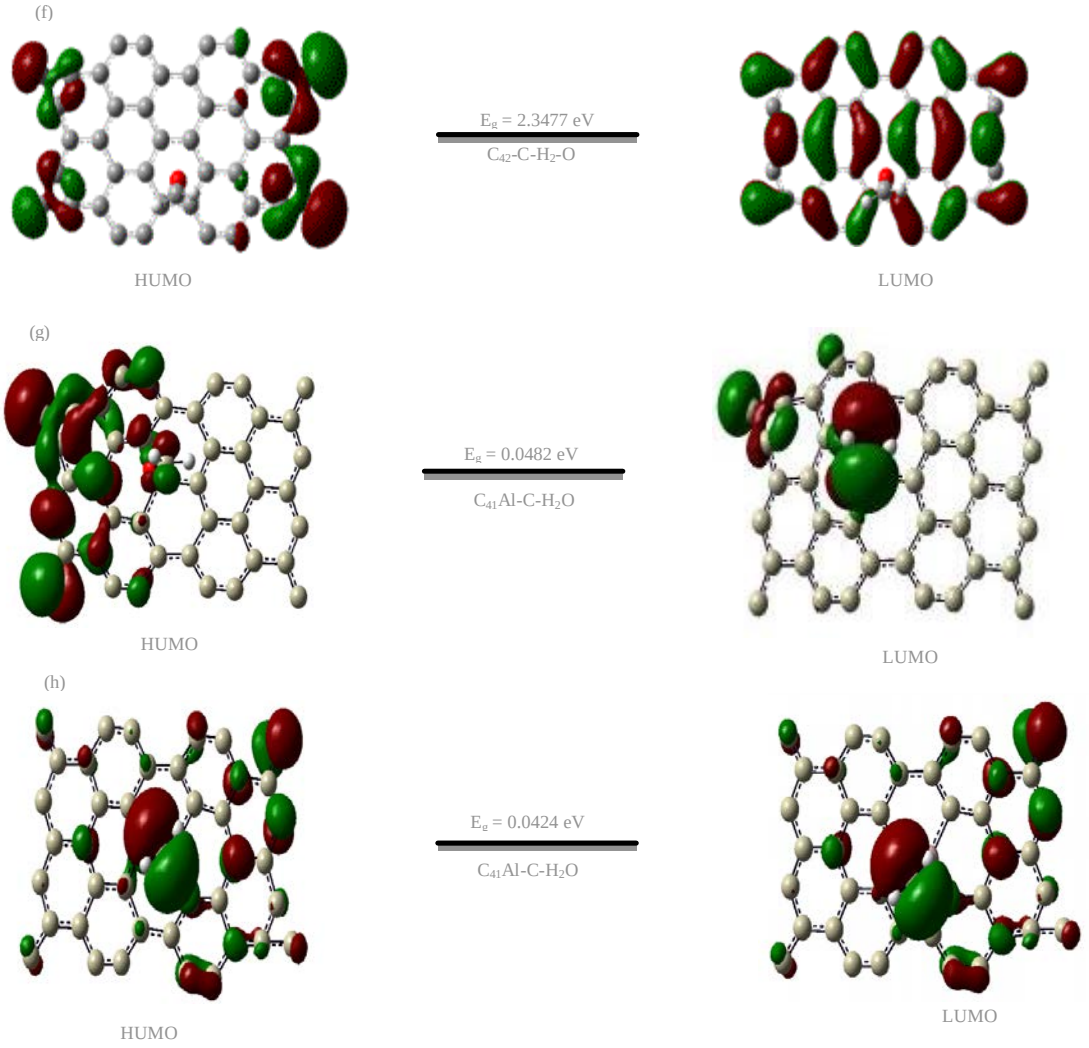

Fig. 2: The DFT calculation of HOMO and LUMO shapes for studied CH_2O adsorption molecules

CH_2O on the C-atom PG, $C_{41}X$, (X = B, N, Al) are (12.587, 0.725, 15.917 and 0.930 eV, respectively. While (E_{ad}) of CH_2O on the center ring of the C-atom PG, $C_{41}X$, (X = B, N, Al) are 12.6, 0.965, 14.01 and 0.752 eV, respectively, E_{ad} of a gas atom are found using (Eq. 3), However, the E_g of CH_2O on the C-atom PG, $C_{41}X$ (X = B, N, Al) are 2.345, 0.252, 1.868 and 0.048 eV, respectively. While (E_g) of CH_2 O on the center ring of the C-atom PG, $C_{41}X$ (X = B, N, Al) are 2.347, 0.758, 0.347 and 0.042 eV, respectively, E_g of a gas atom are found using (Eq. 2) while the E_g for adsorption of CH_2O on B-doped grapheme, N-doped graphene and Al-doped graphene are smaller than those of B-doped graphene N-doped graphene and Al-doped graphene, respectively which indicates that the E_g decreases with the adsorption of CH_2O on B-doped graphene N-doped graphene and Al-doped graphene. One can see from the overall results that are displayed in Table 1 that E_{ad} of PG and N-doped graphene is larger than E_{ad} for another systems. The E_{ad} of Al-doped graphene (on atom Al and center ring) is larger than 1 eV, corresponding to strong chemisorption . The E_{ad} B-doped graphene (on atom B and center ring) is smaller than 0.5 eV, corresponding to weak physisorption (Feng *et al*., 2014). The E_{ad} for B-doped graphene (0.273 eV) and the center ring B-doped graphene (0.315 eV) are in agreement with the previous results (Shwartz, 2012; Kondrashov *et al*., 2016). In general, the E_{ad} in the results indicates that Al-doped graphene is strongly reactive to molecule CH_2O, the E_{ad} is 1.261 and 1.527 $eV_{center\ ring}$ corresponding to a strong chemisorption. Therefore, due to gas slow desorption from Al-doped graphene, the Al-doped graphene is not suitable as a sensor of CH_2O. Nevertheless, Al-doped graphene could catalyst or activate this adsorbate due to the strong

interaction, suggesting the possibility of Al-doped graphene as a catalyst. For B-doped graphene and (B-doped graphene)$_{center\ ring}$) the binding strength of CH_2O with B-doped graphene and(B-doped graphene)$_{center\ ring}$) are E_{ad} of 0.273and 0.315 eV, respectively, the results E_{ad} for B-doped graphene are consistent with those reported in other studies (Shokuhi *et al*., 2016). Thus, B-doped graphene and (B-doped graphene)$_{center\ ring}$) can be used to detect CH_2O, since, the adsorption-desorption equilibrium of CH_2O, B-doped graphene and (B-doped graphene)$_{center\ ring}$) are easily built. Table 1 Structural and electronic properties of adsorption of CH_2O molecules on PG, B-doped graphene, N-doped graphene and Al-doped grapheme.

Table 1 indicates that E_{HOMO} and E_{LUMO} for adsorption CH_2O on B-doped graphene, Al-doped graphene(on the atom and the centr ring) are smaller than the PG, N-doped graphene. We found that high value of E_{HOMO} is -6.347 eV, this value indicates a tendency of the molecule to donate electrons while the lower the value of E_{LUMO} is - 3.999 eV, this value indicates a tendency of the molecule to accept electrons.

Figure 2 DFT calculation of HOMO and LUMO shapes for studied CH_2O adsorption molecules. In the molecule C_{41} lobes in the HOMO are concentrated on the right and few numbers on the left. and LUMO are concentrated on almost all atoms. We observe that the lobes $C_{41}B$ lobes in the HOMO are concentrated on the left and right and LUMO are concentrated on almost all atoms in the molecule $C_{41}B$ (center) lobes in the HOMO are concentrated on the right only and LUMO are concentrated on the left only.

In the molecule $C_{41}N$ lobes in the HOMO are concentrated on the right only and LUMO are concentrated on almost all atoms in the molecule $C_{41}Ngas_{center}$) lobes in the HOMO are concentrated on the right and left and LUMO are concentrated on almost all atoms. In the molecule $C_{41}Al$ lobes in the HOMO are concentrated on the right only and LUMO are concentrated on the top right. In the molecule $C_{41}Al$ gas (center) lobes in the HOMO are concentrated on the right only and LUMO.

CONCLUSION

The conclusion of the present study adsorption of gases CH_2O can be summarized as follows.

For adsorption of gas CH_2O: Doped graphene ($C_{41}X$ (X = B, N, Al) molecules leads to a change to the structure and electronic properties of pristine graphene C_{42}. The bond lengths of optimised structure for adsorbed system decrease with increasing of number of electrons in the elements. The calculated E_{Tot} for all systems increases (in magnitude) with increasing the number of atoms. There is no distortion in the planar structure of graphene sheet in the case of doping boron, nitrogen and aluminium atoms in graphene sheet.

The adsorption of gas molecules on B-doped graphene and center ring undergoes a weak physisorption interaction with E_{ad} for (0.273) (0.315 $_{center\ ring}$) eV, thus, B-doped grapheme can be used to detecting gas molecule CH_2O. B-doped graphene on atom and center ring can be used as a good sensor for CH_2O and (PG, N, Al) doped graphene not suitable for usage as a gas sensor for CH_2O.

The adsorption of gas molecule CH_2O on (PG, N, Al)-doped graphene and center ring undergo in a strong chemisorption interaction with E_{ad} (12.587, 15.917, 1.261) eV and (12.6, 14.01, 1.527)$_{center}$) eV, so, it presumably unsuitable for usage as a gas sensor for these gas, the values of E_g decrease for adsorbed ($C_{41}X$ (X = B, N, Al) doped graphene on atom and center ring. The electronic properties of graphene can be modified by molecules adsorption, boron, nitrogen and aluminium doping one atom.

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