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# TITLE: Allicin on single-walled carbon nanotubes zigzag physical adsorption using density functional theory.

Mehdi Ghaffari Moghaddam

*Department of Chemistry, Faculty of Science, University of Abhar, Zanjan, Iran*
Email: M.gh.moghaddam1990@gmail.com

**Abstract:** Since the discovery of carbon nanotubes, extensive researches have done to find the ability of these nanostructures in multiple sciences. One of these areas, is the physical adsorption of important molecules, especially as Allicin, including molecules that have medical applications. One of the ways how Allicin as molecules can be separated and recognized probably is the study of its interactions by carbon The present study tries to investigate the interaction of Allicin with carbon nanotub as zigzag using .nanotubes quantum chemistry calculations. For this purpose, the method of density functional theory is applied and (6,0), included72 atoms were used. Allicin in different directions interacted with nanotub while the energy and minimum distances of adsorption were calculated. The results have shown that the (6,0) SWCNT, adsorbed Allicin from a part of sulfur, and of course with the nearest distance,. However, further studies should be done in this case.

***Keywords:***. 1- Allicin 2- CNT **3**- DFT **4**- VdW

## Introduction

1. Introduction

1-1 Carbon nanotubes

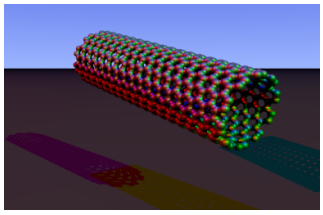


Fig 1-1: three-dimensional view of carbon nanotubes

The nature of the element carbon naturally in the solid state in the form of diamond and graphite The third type is currently produced in the laboratory of nanotechnology are carbon nanotubes .
The difference properties of carbon nanotubes to replace species that has caused a lot of material in the industry and cause massive upheaval in the material world
2-1: The discovery of carbon nanotubesIn the mid-1980s, Kroto, Small and his colleagues were able to use laser vaporization of graphite in a joint investigation, A large family of 60 carbon atoms for sustainable intensive clusters using mass spectrometry sample vaporized carbon discover, The molecules of similar geometric surfaces were designed and manufactured by Buckminster And called fullerenes were read. The most famous and enduring yet Structure which is produced fullerenes is C60. (C represents carbon and carbon-60 atoms in a fullerene molecule are introduced a number), which is also known as a buckyball is made (Figure 2-1).

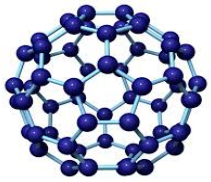


Fig 2-1: fullerenes (C60)

In 1991, Iijima and his colleagues have been studying the carbon residue of an arc between graphite electrodes were Discharge Using transmission electron microscopy (TEM) with high resolution (HRTEM), carbon disciplines and winding observe screw (Figure 3-1).

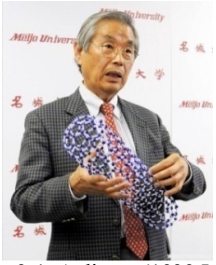


Figure 3-1: Ayljyma (1939 Japan)

Carbon nanotubes are a new breed of nano-structures composed of carbon atoms have been significantly [1]. Carbon nanotubes as a type of nanomaterial attracted a lot of attention limitations [2]. Because of the unique properties of mechanical, chemical and electrical carbon nanotubes [3] Its distinctive properties such as: the ability to accumulate analyte, to minimize the level of fouling and electro-catalytic activity for electrochemical measurement are awesome [4].

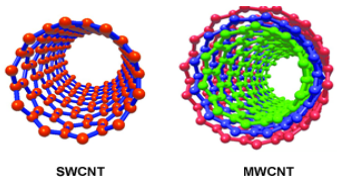



Figure 4-1: single-walled and multi-walled nanotubes view

Single-walled carbon nanotubes includes two types of nanotubes (SWCNT) and multi-walled nano-tubes (MWCNT) (Figure 4-1), In 1991 and 1993, respectively, which were discovered by Iijima [6-5]. Single-walled nanotubes are the most simple geometry and a diameter of about 0.8 and 2 nm.

1-3-1- Single-walled carbon nanotubes (SWNT)

Single-walled carbon nanotubes of carbon just one Sakhtarsadh (sheet of regular hexagons) were formed. Some projections indicate that single-walled conductor or semiconductor can be. The high electrical conductivity depends on the exact geometry of the carbon atoms. Since the beginning of their work on single-walled as a one-dimensional phenomenon were called to the stage to stage this theory has evolved.

Due to the angle of torsion pages graphene, single-walled nanotubes are divided into two general categories chiral Vakayral. CNT carbon nanotube is Ghyrkayral mirror image of the original structure is the same. Single-walled carbon nanotubes-sheets of graphite which are wrapped to form a layer with nano dimensions [7].

Single-walled carbon nanotubes according to the arrangement of carbon atoms pipe section into three major categories armrest and metallic properties that are chiral and zigzag is divided semiconductor properties [8].

2-3-1- multi-walled carbon nanotubes (MWCNT)

Single-walled carbon nanotubes with additional graphene tubes surrounding a central material called multi-walled nanotubes [9]. Multi-walled carbon nanotubes are always electrically conductive [10].

Multiwalled carbon nanotubes (substitute carbon black) in color powders. One of the disadvantages of the single-walled multiwalled nanotubes is that less is strengthening because they are weak internal page links.

4.1:.Armatureandzigzag CNTs

Due to the angle of torsion pages graphene, single-walled nanotubes are divided into two general categories chiral Vakayral. Ghyrkayral carbon nanotube nanotubes that are identical mirror image of the original structure (Figure 5-1).

There are two kinds of chiral nanotubes: Zigzag and the armature. The name comes from the shape of the cross-section of them. So there are three types of single-walled carbon nanotubes. To roll the sheets of graphene and nanotubes diameter of two integers n and m can be achieved.

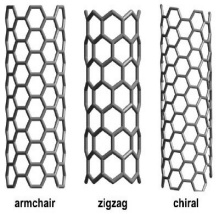



Fig 5-1: Types of single-walled nanotubes

5-1:Zigzag Carbon Nanotubes

The chiral vector is equal to zero, one of its components, such as vector (6, 0) of the recurring units such as (Figure 6-1) are formed. The zigzag vectors are vectors in the class. It is named because of the appearance of this unit. The English name of the vectors, the zigzag.

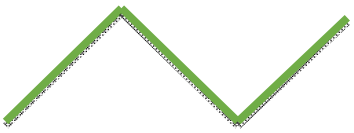


Fig 6-1: repeat unit for chiral vector (6, 0) (zigzag)

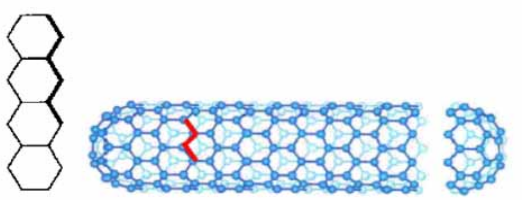


Figure 7-1: atoms joined together to create the kind of zig-zag shape.

Sharp zigzag nanotubes are paramagnetic and gradually lose its magnetic properties. Highly dependent on the length - radius - temperature and strong magnetic flux.

2 - Methods of Computational Chemistry

1-2: density functional theory (DFT)

DFT theory within the framework of quantum mechanics to study the electronic structure of many-particle system. In this theory, the introduction of universal energy functional variation of the electron characteristics of the material (in this case the electron density) is obtained.

Density functional theory, in fact, a useful tool for calculating the ground state energy [11] And density distributions [12] Molecular atoms and solids, particularly for systems involving a large number of atoms or molecules is With this theory can be accurate density and energy of the ground state electron systems under the influence of an external potential are calculated. Moreover, by using density functional theory can be non-Hamgin systems with different interactions can be studied. Simple-most used approximation is the local density approximation LDA [13]. With this theory can be single-atom Schrödinger equation with single-atom potential correlation with the potential LDA exchange earned and calculated the density [14].

The wave function for acease-electron interaction $\psi(r_1, r_2, \dots r_N)$
Where i've been r_1 spatial coordinates and spin of electrons. Schrödinger equation is answered below.
Relevance1-2; $(\hat{T}_e + \hat{H}_{ee} + \hat{H}_{ne})\psi(r_1, r_2, \dots r_N) = E\ \psi(r_1, r_2, \dots r_N)$
Density functional theory based on the principle that every property of a few interacting particles can be A function of the density of the ground state (r) n0 considered and its density is a function of the location swing. Prove the existence of such a function in the work Hohenberg Kahn and Mermin [15].
The basic rules of order by density functional theory (Hohenberg and Kohn) and (Cohen and dinner) in the years 1964 and 1965 were presented. Cases Hohenberg - Kohn show That all the properties of the ground state of a cease-electron interaction can be obtained from the density of the ground state, As a result, many devices electron ground state energy function of the density of variational principle comply. Cohen case - you represent the ground state electron density is exclusively determined by the total energy of a system. Mathematically, the electron density ρ at a point in real Fzary by Coordinates x. y. z. Defined by function $\rho = \rho(x. y. z)$
Displays the total energy of the system, E can be defined as a function of electron density.
Relevance 2-2; $E = E < \rho(X. Y. Z) >$
To determine the energy can be divided into three categories as follows:.
Relevance 3-2; $E[\rho] = T[\rho] + U[\rho] + Exc[\rho]$
The (T) kinetic energy of electrons . Coulomb energy U, Exc energy exchange between the electron - electron. Coulomb energy is expressed by the following equation:
Relevance 4-2; U = U ne + Unn +Uee
The U ne Uee, Unn, and Unn represent the attraction between electrons and nuclei, electrons and electron repulsion -The core are repulsive.

2.2- interactions between particles based on molecular mechanics

Intermolecular interactions (non-hybrid) models that form the potential use of this potential is as follows (a combination of potential and electrostatic potential Lnard- Jones):

Relevance 5-2; $u(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$

To calculate intermolecular interactions, the combination of potential and electrostatic potential is used Lnard-Jones. Lnardjvnz parameters (ε and σ) and atomic charges adsorb gases from the force fields to be earned.

1-2-2- The van der Waals (short-range)

As mentioned earlier, Benard Jones parameters (ε and σ) to adsorb and absorbent fields are proudly. To calculate the molecular interactions between absorbent and adsorbent in the simulation All parameters Benard - Jones by mixing the Lorentz - Berthelot determined. The equations of the form are as follows:

Relevance 6-2; $\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}), \varepsilon = \sqrt{\varepsilon_{ij}\varepsilon_{ij}}$

2-2-2; The electrostatic (range - Long)

The second term potential equation (2-11), Coulomb equation for calculating the electrostatic forces are:

Relevance7-2; $E_{coul} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{\infty}\frac{q_i q_j}{r_{ij}}$

Korea radius Rc of the equation when system loads to be cut and in case if $N \to \infty$ for a position defined and conditionally convergent.

3.2 periodic boundary conditions

The simulation system with more than a few tens of thousands of computers are typically very time consuming and not spend for larger systems. To solve the problem of periodic boundary conditions are used. In this situation, a system containing N atoms in a cube can be considered. These systems are surface atoms to cause the situation that certain behavior show and the main difference is small systems to large systems. Several cubes are placed around the basic cube which is actually a virtual copy of the preliminary system, so that the effect is removed. If an atom of a cube out of funds, with the same speed from the other side of the cube. By this method, boundary conditions simulation system will be large system will have the same treatment. In (Figure 2-1) this behavior is observed.

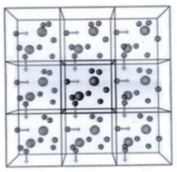


Fig 1-2: periodic boundary conditions

3. Results

```
LatticeConstant     1.00 Ang
%block LatticeVectors
  20.00000000    0.00000000    0.00000000
  0.00000000   25.00000000    0.00000000
  0.00000000    0.00000000   20.00000000
%endblock LatticeVectors
MeshCutoff          125  Ry
%block kgrid_Monkhorst_Pack
  1   0   0     0.0
  0   1   0     0.0
  0   0   1     0.0
%endblock kgrid_Monkhorst_Pack
xc.functional   GGA   # Default value
xc.authors      revPBE   # Default value
#*****************************************
*****
PAO.EnergyShift    110  meV
PAO.SplitNorm    0.30
PAO.SplitNormH   0.50
```

PAO.SoftDefault true
PAO.SoftPotential 50.0 Ry
PAO.SoftInnerRadius 0.80
PAO.BasisSize DZP

***1***.3 Interaction Results CNT (6‹0) & ALLICIN

In Figure1-3, three-dimensional images of allicin can be viewed.

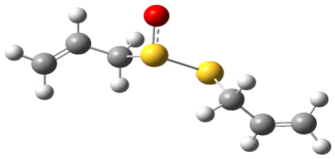


Fig 1-3: three-dimensional images of allicin

Single-walled carbon nanotube three-dimensional schematic in Figure 2-3 (6, 0) can be seen The ends of the nanotubes by hydrogen atoms have been linked to the cause of this could be due to repeated intermittent nanotubes The hydrogen atom cut nanotubes and the nanotube block to prevent the recurrence of intermittent endless.

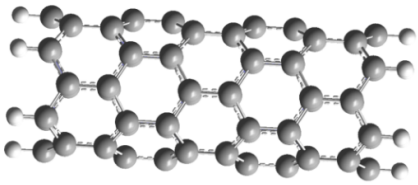


Fig 2-3: three-dimensional image of carbon nanotubes (6,0)

2.3 of allicin molecule functional groups

At the end of a three functional group single-walled carbon nanotubes for molecular absorption by allicin is used in different situations In order to separate each in various positions (Figure 3-3).

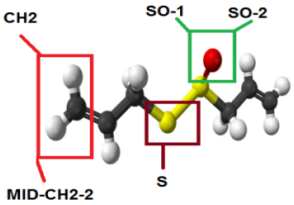



Fig 3-3: Overview of functional groups allicin

Table 3-1: Introduction position and functional groups of allicin

Allicin molecules and single-walled carbon nanotubes from 5 to (6,0) are close.

| Number | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| position | CH2 | MID-CH2-2 | S | SO-1 | SO-2 |

In position 1 hydrogen from the middle of the ring hexagonal carbon nanotubes is close to the outer surface (Figure 4-3). In position 2 hydrogen from the carbon nanotube approaches (Figure 5-3). Allicin, a sulfur atom at position 3 from the outer surface of the nanotube approaches (Figure6-3). In position four oxygen atoms of allicin from the outer surface of the carbon nanotubes is close to the hexagonal ring (Figure7-3). As oxygen atom at position 5 to the outer surface of the ring hexagonal nanotubes and carbon nanotube approaches (Figure 8-3).

DistanceÅ =3.21

Angle° = 98.204

E(CNT(6,6)&ALLICIN) (eV)= -14081.393797

H77

C23

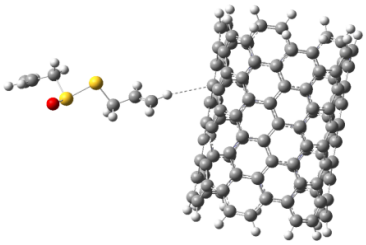


Figure 4-3: Position 1 allicin interaction of the hydrogen with carbon atoms of carbon nanotubes

DistanceÅ =2.85

Angle° = 112.78

E(CNT(6,6)&ALLICIN) (eV)= -14081.351362

H87

H102

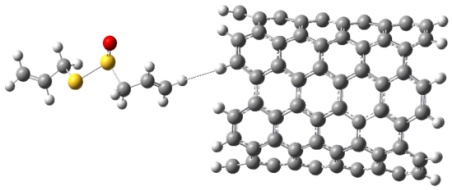


Fig 5-3: Position 2 allicin interaction of the hydrogen with hydrogen from carbon nanotubes

DistanceÅ =2.73

Angle° = 152.77

E(CNT(6,6)&ALLICIN) (eV)= -14081.489992

O91

c39

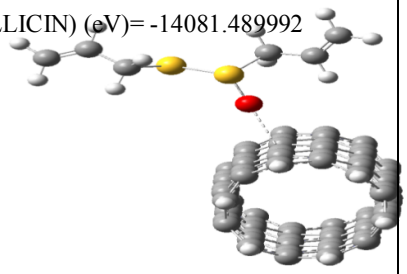


Fig 8-3: Location 5 of garlic, allicin oxygen atom with carbon nanotubes (inside the 6-sided ring)

DistanceÅ =3.27

Angle° = 131.66

E(CNT(6,6)&ALLICIN) (eV)= -14081.468500

S89

C62

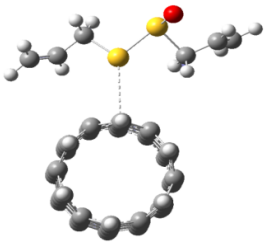


Fig 6-3: Position 3 allicin from garlic, sulfur, carbon nanotubes

Table 2-3: allicin and closest link between carbon nanotube uptake in 5 positions

| 5 | 4 | 3 | 2 | 1 | Number |
|---|---|---|---|---|---|
| SO-2 | SO-1 | S | MID-$CH_2$-2 | $CH_2$ | position |
| $C_{39}$ | $C_{58}$ | $C_{62}$ | $H_{102}$ | $C_{23}$ | $CNT_{6.0}$ |
| $O_{91}$ | $O_{91}$ | $S_{89}$ | $H_{87}$ | $H_{77}$ | Allicin |
| 2.73 | 2.64 | 3.27 | 2.85 | 3.21 | Distance (Å) |

DistanceÅ =2.64

Angle° = 146.96

E(CNT(6,6)&ALLICIN) (eV)= -14081.277157

O91

C58

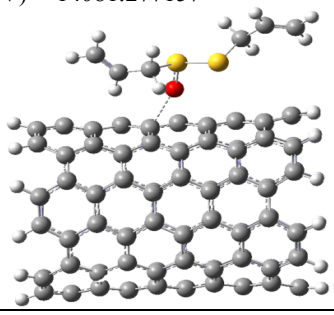


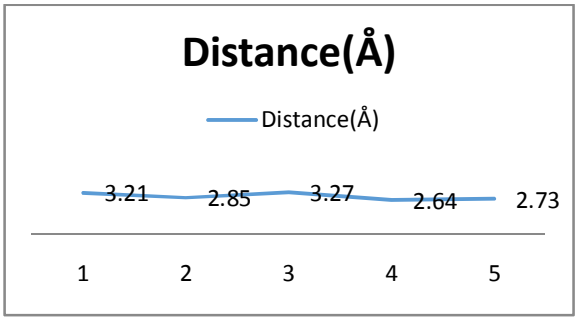
Fig 7-3: position 4 of the carbon atoms of oxygen with carbon nanotubes allicin (the 6-sided carbon rings)

2.3 functional groups at positions absorb bond length

Table 3.3: Minimum distance of each link

| Number | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Distance (Å) | 3.21 | 2.85 | 3.27 | 2.64 | 2.73 |

Chart 1-3: the shortest distance between the link and allicin interaction of carbon nanotubes (0,6)




The shortest distance between functional groups absorb in position 4 (Å 81/2) and position 2 and 5(273 Å)also seen close.

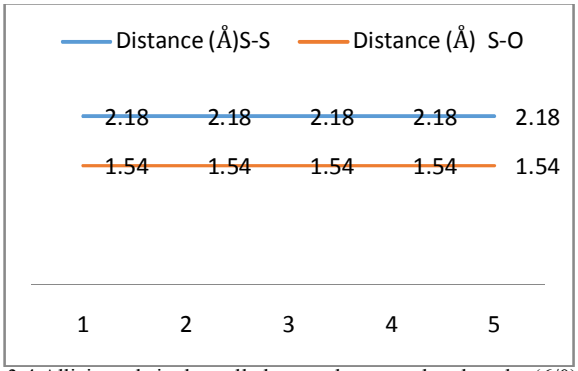
3.3 allicin molecules bond length between atoms in different positions absorption

In connection with this bond length sulfur - sulfur, oxygen and sulfur allicin molecule absorption was measured at different positions (Table4-3) remains permalink distance and direction of impact absorption during the transplant sulfur - sulfur and oxygen - no sulfur (chart 3-3)

Table 4-3: The bond oxygen atoms with oxygen and oxygenSulfur

| Number | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Distance(Å)S – S | 2.18 | 2.18 | 2.18 | 2.18 | 2.18 |
| Distance(Å)S – O | 1.54 | 1.54 | 1.54 | 1.54 | 1.54 |

chart 3-3: oxygen atoms with oxygen and oxygen-sulfur bond length




3.4.Allicin and single-walled nanotube atoms bond angle (6/0)

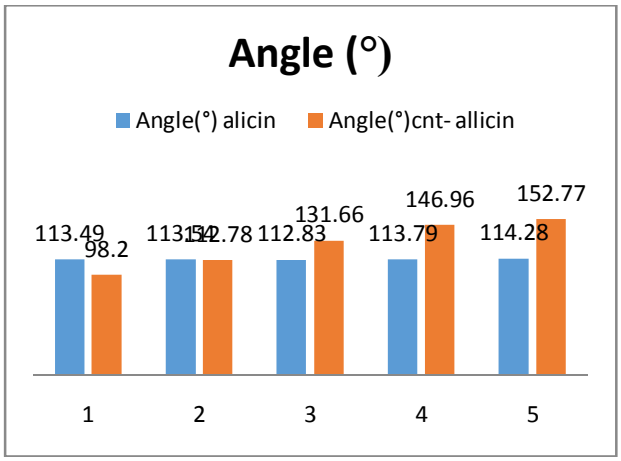
This is the angle between the atoms (oxygen - sulfur - sulfur) and angle of allicin molecules absorb allicin bond between the carbon nanotubes( 6.0) measured in different situations (see Table 5-3)

Table 5-3: angle between the link and allicin atoms of carbon nanotubes (6,0)

| Number | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Angle(°) Allicin S189 – S190 – O191 | 113.490 | 113.54 | 112.83 | 113.77 | 114.28 |
| Angle(°) CNT-Allicin | C23-H76-C75 | H102-H87-C85 | C62-S89-S90 | C58-O91-S90 | C39-O91-S90 |
| | 98.204 | 112.78 | 131.66 | 146.96 | 146.42 |

The angle between the atoms in position 5, the angle between the atoms allicin allicin and allicin angle between the interacting atoms and carbon nanotubes (0,6) has its maximum value.

Figure 3-3: the angle between the link and allicin atoms of carbon nanotubes (6,0)




5.3 energy

Vandvalsy allicin absorbed energy equation and density functional theory (DFT) bond length and bond angle with respect to allicin with carbon nanotubes (6.0) is calculated. Calculated according to the following equation.

Relevance 1-3;

Eads(eV)= E(CNT6,0 – Allicin ) - E CNT6,0 -E Allicin

E CNT6.0 = - 11864.644138 (eV )

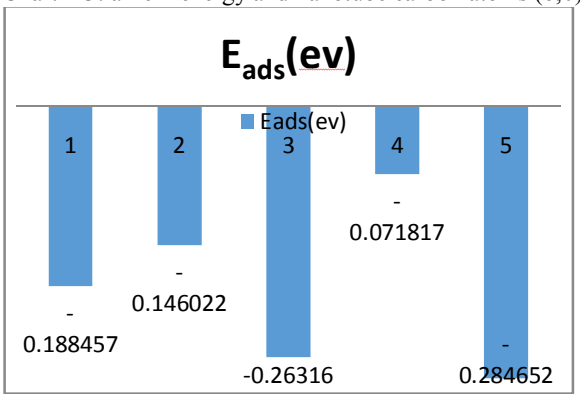
E Allicin = - 2216.561203 (eV )

Table 6-3: allicin and energy between the atoms of carbon nanotubes in different situations

| Number | 1 | 2 | 3 | 4 | |
|---|---|---|---|---|---|
| Position | CH2 | MID-CH2-2 | S | SO-1 | SO |
| E(CNT6.0 – Allicin ) (ev) | 14081.393797- | 14081.351362- | 14081.4-68500 | 14081.2771-57 | 14 1.489-992 |
| Eads (ev) | 0.1884-57 | 0.1460-22 | 0.26316- | 0.071-817 | 0.284-652 |

After calculating the total energy of the interaction between single-walled carbon nanotubes allicin and (0.6) absorbed at different positions (Table 8-6) is considered the lowest and most stable interaction energy is absorbed in the position 3 and position 5 position 4 is also noteworthy unstable position (chart 4-3).

Chart 4-3: allicin energy and nanotube carbon atoms (6,0)




6.3 Calculations density of states (DOS) for the absorption of allicin by CNT (6,0)

To understand the behavior of the electronic orbitals of single-walled carbon nanotubes and find out the nature of the allicin and (6.0) that the binding density of states (DOS) for blending system SWCNT / ALLCIIN with DOS compare the individual parts.

To calculate the density of single-walled nanotubes interact with allicin (6.0) that the 5 one orientation orientation is acceptable that the review mode DOS (Figure 8-3) Position 5 found that allicin molecules absorb DOS near the Fermi level at the level of single-walled carbon nanotubes (6.0) does not affect the sub-zero energy-Dhd.tnha very small changes can be seen that the results show that allicin molecules absorb carbon single-walled nanotubes (6.0) no effect on the distribution of electronic charge is not carbon nanotube atoms.

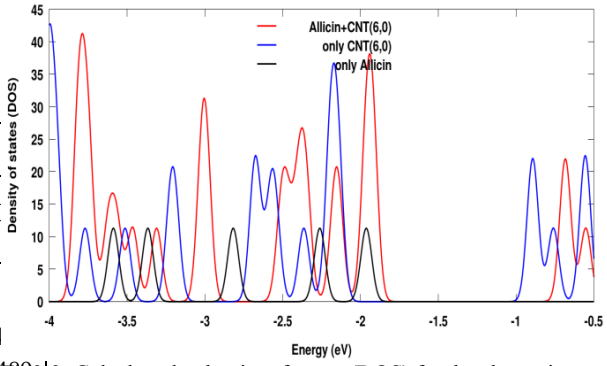



Fig1-3: Calculate the density of states (DOS) for the absorption of allicin in nanotubes (Position 5)

4- Conclusion

Viewed as allicin star turn is closer to Krbnytk walled nanotubes (6.0) from position 5 (Figure1-4) both in terms of link length, the shortest distance and the nearest size (2/73 Å) images. Most angle than the atoms of allicin (114/280 degrees) Vbrhmknsh allicin nanotubes (152/77 °) is noteworthy that position 4 is also inclined but inclined position 4 may be caused by the interaction of very high and significant energy is extremely unstable position 4 position 4 Lzamy be ignored. In terms of energy and a more sustainable energy positions 3 and 5 position 3 of the criterion (distance and angle) is unacceptable and energy can be the result of interactions is high.

The closest and most stable energy angle and position 5 (Figure1-4) is more favorable, then it is better interaction between allicin Vnanvlvlh single-walled carbon (6.0) in the fifth position and calculated approach DOS indicated that position 5 allicin has little effect on the optical properties of single-walled carbon nanotubes (6.0) does not.

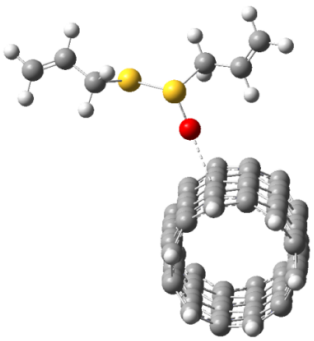


Fig1-4: allicin approach to carbon nanotubes (6,0) (Position 5)

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