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VARIOUS TECHNOLOGICAL PROCESSES

# Thermodynamic Study of PCB-153 Passing into Single Walled Carbon Nanotube (8,8)[1]

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**Abstract**—Polychlorinated biphenyl (PCBs) are high resistant pollutants which cause adverse health effects in recent years. The accumulation of these toxic compounds in the food chain lead to oxidative stress in various ecosystems. Detection, absorption, and elimination of them are an environmental priority. Passing of PCB-153 through the armchair single walled carbon nanotube (SWNT) (8,8) were investigated by MNDO in semi-empirical quantum method. Calculated electrical and thermodynamic properties show a sudden change in the middle of the tube which may act as a trap for the studied pollutant. The results indicated the nanotube has considerable ability to interact with PCB-153 and cause its degradation. According to calculated thermodynamic parameters through the molecular modeling, it is expected that single wall carbon nanotube is a candidate in remediation of PCBs as well as in gas sensor devices for detection of them. The median tube is a place for trapping pollutants.

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## INTRODUCTION

Although production of polychlorinated biphenyls (PCBs) was banned since the 1970s, but due to their persistent to biodegradation, these carcinogen chemicals remained in the ecosystems [1]. These compounds can transfer from environment into the organisms and accumulate during the food chains in the fat tissues. According to performed studies on pathogenesis potentials of PCBs, they cause to insufficiencies by oxidative stresses [2, 3]. Today it is found that exposure to the congeners of PCBs could lead to various types of diseases especially to brain disorders and cancers [4, 5]. In recent decades degradation of these harmful pollutants was been an environmental concern because of mentioned adverse effects.

Carbon nanotubes (CNTs) particularly of single walled armchair types were inquired for environmental applications including environmental monitoring by removal and detection of pollutants as well as energy conversion and storage [6]. Surface modifications of CNTs such as adsorption of gaseous species have a considerable potential to show strong feedbacks. Recently this high sensitivity causes that CNTs receive remarkable attentions in gas sensors contexts [7, 8]. On the other hand CNTs are capable to removal of volatile organic compounds (VOCs) containing chlorine. For example they were used as a sorbent for dioxin degradation and 1,2-dichlorobenzene (DCB) [9, 10]. Because of unique properties, single walled carbon nanotubes (SWNTs) are investigated for detection and elimination of different pollutants [11].

Many theoretical researches have studied remediation potential of the nanostructures at exposure to various contaminations in aquatic and gaseous phases. The obtained results show that carbon nanotubes because of special features are able to provide a suitable surface for conversion of highly toxic pollutants to low risk products [12–14]. The current research tends to simulate passing of PCB-153 through SWNT (8,8) by computational methods.

## THE COMPUTATIONAL METHOD

In the work we simulated passing of 2,4,5,2',4',5'-hexachlorobiphenyl (PCB-153) through SWNT [armchair

[1] The text was submitted by the authors in English.

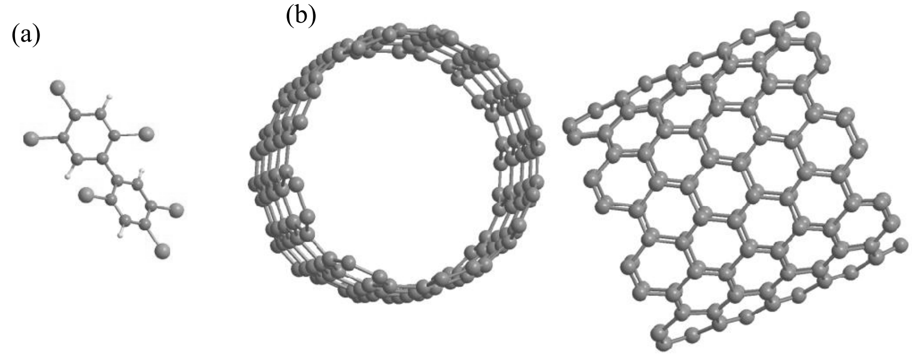


**Fig. 1.** The ball and stick model of optimized geometrical structure: (a) PCB-153, (b) single wall carbon nanotube (8,8).

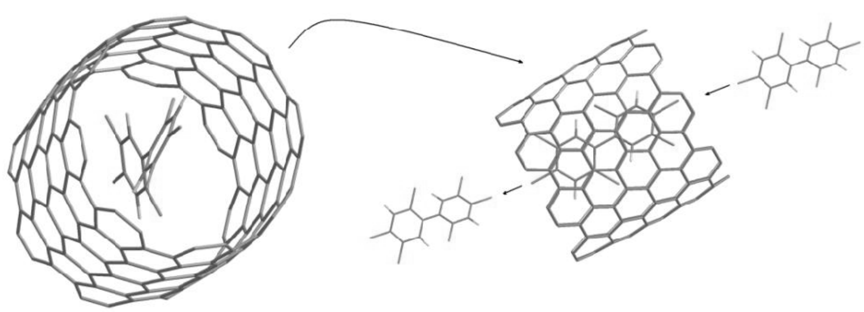

**Fig. 2.** The stick models of configuration of PCB-153 passing into SWNT (8,8).

(8, 8)]. Because of four *para* and *meta* positions are occupied by chlorines, this PCB is considerably toxic [15]. A density function theory (DFT) calculations including geometry optimizations were done for studied PCB and nanotube by GAMESS program package. All of the structures were optimized at B3LYP/6-31G level. As well as for molecular energies determination of PCB interaction with CNT we utilized MNDO as a semi-empirical quantum method. MNDO method is widely used for calculation of heat of formation, ionization energies, and dipole moments. By obtained parameters of the simulated interaction, calculation of the thermodynamic parameters will be possible. It should be noted passing of PCB within nanotube was simulated in room temperature and five distances.

## RESULTS AND DISCUSSION

PCBs are stable and low biodegradable compounds. These persistent chemicals are able to produce radicals and cause oxidative stress in various organs [16]. Adsorption and neutralization of these toxic chemicals by green technologies such as nanotech may be a novel approach in their remediation. At first the Z-matrix files for CNT (8,8) and PCB-153 were produced and then their structures were optimized by B3LYP/6-31G in Gaussian software working under linux. Afterwards passing of the PCB through the central axis of the nanotube at five steps was simulated. The interaction between species under study was calculated using semi-empirical method. The thermodynamic properties of mentioned interaction were listed in Table 1. All of the parameters in Table 1 were calculated by MNDO method.

Based on Fig. 3 the passing of the PCB across from the nanotube increases the total energy. In middle of the tube length, the slope decreases significantly, suggesting adsorption of the pollutant on the nanotube internal surface.

As shown in Table 1, free Gibbs energy for PCB-153 passing across from the nanotube in the all of the distances is negative and in the fourth step reaches to the minimum value. In this step SWNT envelops the pollutants completely.

Conformations with low dipole moments may be a possible reason for bioaccumulation of PCB in adipose tissue [17]. Based on Table 1 dipole moments along the tube length increasing until at 12.75 Å show a significant decrease that indicates a structural symmetry perturbation. On the other hands Figures 3–5 demonstrate that the binding, nuclear and total energies increase and in

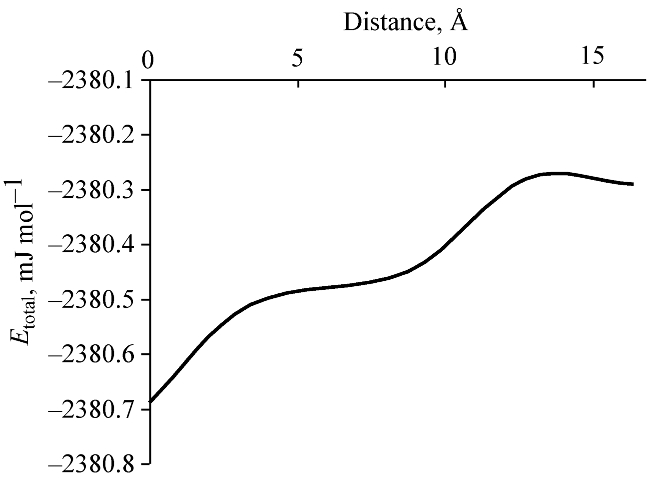


**Fig. 3**.The total energy $E_{total}$ of PCB-153 passing across from SWNT (8,8).

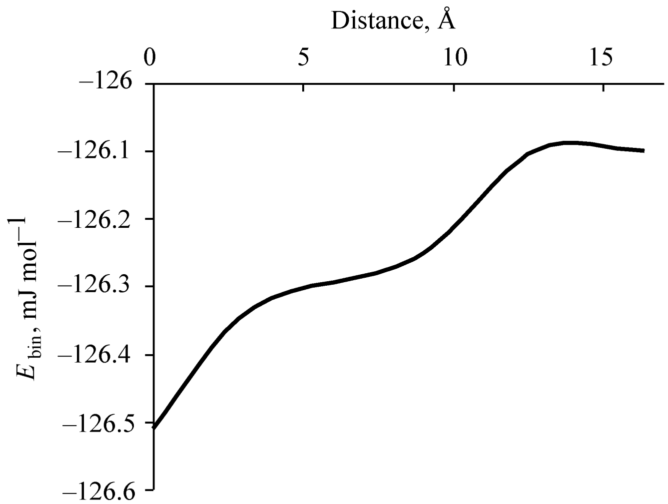


**Fig. 4**.The binding energy $E_{bin}$ of PCB-153 passing across from SWNT (8,8).

fourth stage they are in the maximum value. Variations of binding and total energies are the same. Figure 4 shows structural change in the middle. As a result, the reaction of the pollutant with nanotube, which contains adsorbed and degraded PCB, will be an imminent event.

The conductance of nanotube increases when PCB-153 passes across from the nanotube and in the fourth step it is at the top. On the other words, PCB passing through nanotube enhances nanotube conductivity. These variations in electrical properties suggest this nanostructure is able to detect PCB-153 in the environment. The electrical resistance was calculated by the conductivity as:

$$E_{elec} = RI, \quad (1)$$

where $E_{elec}$ (V) is electrical energy, $I$ (A) is electrical intensity, and $R$ (Ω) is electrical resistance. So for calculation of $R$ we can use the following equation:

$$R = \frac{E_{elec}t}{nF}, \quad (2)$$

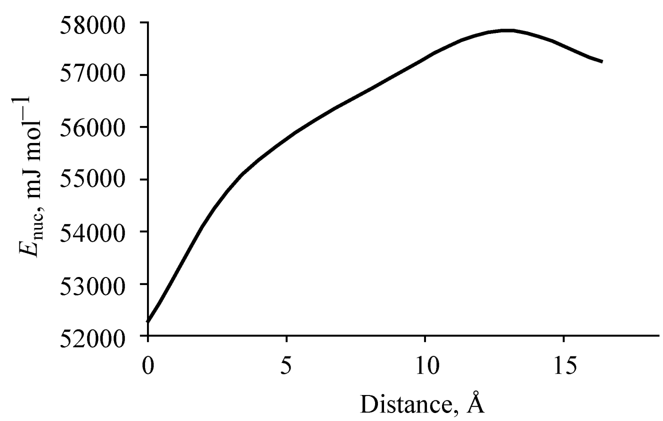


**Fig. 5**.The nucleus energy $E_{nuc}$ of PCB-153 passing across from SWNT (8,8)

where $n$, $F$ and $t$ are number of exchange electrons, Faraday's constant and time (h) of interaction, respectively. By obtaining values for the resistivity, the electrical resistance–time graph was drawn (Fig. 6).

According to Fig. 6 with the entry of the pollutant into the tube, the electrical resistance of the tube decreases

**Table 1.** The thermodynamic properties of PCB-153 passing into SWNT (8, 8) at 298K by MNDO methods

| Distances, Å | $E_{total}$, mJ mol$^{-1}$ | $G_{elec}$, mJ mol$^{-1}$ | Dipole moment, D | RMS kcal mol$^{-1}$ Å$^{-1}$ | $H_f$, mJ mol$^{-1}$ | $E_{bin}$, mJ mol$^{-1}$ | $E_{nuc}$, mJ mol$^{-1}$ | $E_{elec}$, V |
|---|---|---|---|---|---|---|---|---|
| 0 | –2380.69 | –54629.75 | 0.45 | 50.80 | 5.51 | –126.51 | 52249.06 | 566199.41 |
| 3.40 | –2380.51 | –57457.38 | 1.47 | 50.93 | 5.73 | –126.33 | 55076.87 | 595505.88 |
| 8.74 | –2380.45 | –59300.10 | 1.65 | 50.88 | 5.79 | –126.26 | 56919.65 | 614604.37 |
| 12.75 | –2380.28 | –60214.07 | 0.78 | 51.06 | 5.96 | –126.10 | 57833.79 | 624077.05 |
| 16.42 | –2380.29 | –59621.79 | 1.01 | 51.09 | 5.95 | –126.10 | 57241.50 | 617938.41 |

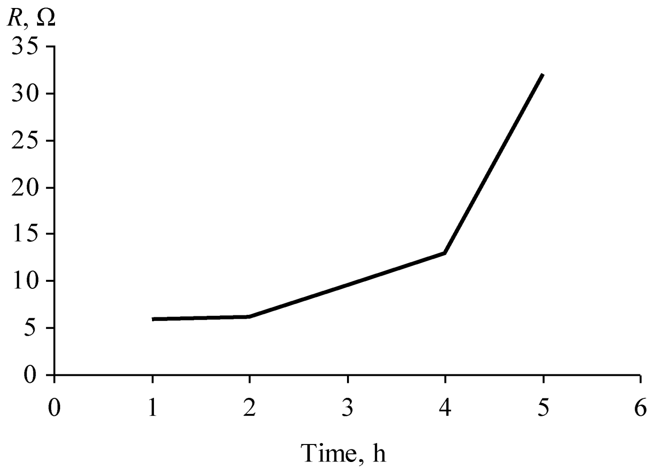


**Fig. 6**. The electronic resistance $R$ (Ω) calculated for passing PCB-153 through SWNT (8,8).

that means an increase of conductivity. Thermodynamic parameters including Gibbs free energy, enthalpy, and entropy differences are calculated using the data of Table 2.

$\Delta G_{elec}$ is negative, so studied passing process is spontaneous. Although $\Delta H_{elec}$ is positive, but because entropy is significantly positive, its effect in investigating the interaction is not remarkable. Consequently, passing of PCB-153 through armchair SWNT (8,8) is favorable in the presence of a little external heat.

## CONCLUSIONS

Since PCBs diffusion to the environment in several decades ago, today their remediation has been a world environmental concern. In this way we assessed adsorption possibility of PCB-153 while passing across from SWNT (8, 8). According to this theoretical study and calculated results, existing interactions between nanotube and PCB have significant potential to lead to PCB-153 degradation. The thermodynamic properties imply that the surface of nanotube can provide a unique surface for removal of this highly toxic chemical. Calculated electrical and thermodynamic parameters showed a sudden change in the middle of the tube that may act as a trap for the studied pollutant. In addition to an increase of the total energy in the fifth step indicates which the nanontube won't repeal the PCB because it is needed to further energize. On the other word after adsorption, absorbent recycling is an endothermic process with more required energy.

**Table 2.** The thermodynamic properties of PCB-153 passing across SWNT (8,8) at 298 K (MNDO methods)

| $\Delta G_{elec}$, mJ mol$^{-1}$ | $\Delta H_{elec}$, mJ mol$^{-1}$ | $\Delta S_{elec}$, mJ K$^{-1}$ mol$^{-1}$ | ln $K$ |
|---|---|---|---|
| –5584.32 | 0.44 | 18.74 | 2253950.23 |

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