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Thermodynamic Study of Polychlorinated Biphenyls Removal by Single-Walled Carbon Nanotube Nano-Sensor Based in Environment: DFT-NMR

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In this study, we have conducted a thermodynamic investigation on converting polychlorinated biphenyls (PCBs) to 4-chlorobenzoic acid, 2-hydroxypenta-2 and 4-dienoic acid using nanosensor-based single-walled carbon nanotube (SWNT). Calculation were done using Gaussian program package. We employed the density functional-based NMR (DFT-NMR) and MNDO semi empirical methods. The polychlorinated biphenyls are one of the most persistent and widespread environmental pollutants. The goal of this work is to improve the detection of surface species of SWNT sensors under their working conditions and using computer calculations and to correlate the sensor signals with relative changes in electric resistance (Ω). We studied the structural and thermodynamic properties as well as the total energy of polychlorinated biphenyl absorption on SWNT at room temperature. When exposed to SWNT-based nanosensors, polychlorinated biphenyls are oxidized into other products including 4-chlorobenzoic acid and 2-hydroxypenta-2,4-dienoic acid. All the geometric structures of this conversion were optimized using B3LYP/6-31G**. Intermediates and transient states of them were optimized using density functional theory (DFT). The results obtained in present study show that electrical conduction and capacitance are increasing when polychlorinated biphenyl is near the surface and when converted to different products.

Key Words: Polychlorinated biphenyls, Nano-structure, Semiconductors, *Ab initio* calculation.

INTRODUCTION

Polychlorinated biphenyls (PCBs) were widely used both in industrial and civil applications. This was mainly because of their advantageous characteristics such as thermal stability, high chemical stability and excellent dielectric properties. Due to their demonstrated toxicity for human and environment, polychlorinated biphenyls are considered as one of the most dangerous pollutants[1]. Polychlorinated biphenyls and dioxins are highly toxic to animal life, particularly birds. Both accumulate in animal (including human) bodies and disrupt the body's hormonal and reproductive systems. Most polychlorinated biphenyls (PCBs) are known to decrease the level of serum thyroid hormone and to increase the activity of hepatic drug-metabolizing enzymes in rats[2].

With the advent of Pd/Fe, an effective catalyst for dechlorination reactions in ambient temperature and pressure, it was applied for river refining from organic chlorinated pollutants during recent years[3,4]. Since this reaction is based on Fe corrosion in water, employing it in oil sources needs extraction process in advance[5,6]. Another method is directed towards the development of a cost effective technology for removing polychlorinated biphenyls from contaminated transformer oils to methanol, so that oil remains usable[7]. In these methods, contaminated aqueous solution (mainly water with a determined volume percent of methanol) reacts with Pd/Fe bimetallic catalyst.

In this study, we used single-walled carbon nanotubes (SWNT) because carbon nanotubes (CNTs) have many distinct properties that may be exploited to develop next generation of sensors. Sensors continue to make significant impact in everyday life. There has been a strong demand for producing highly selective, sensitive, responsive and cost-effective sensors[8], utilization of these properties has led to application of individual nanotubes or ensembles of nanotubes as scanning probes, electron field emission sources, actuators and nanoelectronic devices[9]. Here, we report the realization of individual semi-conducting SWNT (S-SWNT)-based chemical sensors capable of detecting small concentrations of polychlorinated biphenyl molecules.

The main requirements of a good sensor (high sensitivity, fast response, low cost, high volume production and high reliability) are presented in Fig. 1.[10]. The nanotube sensors exhibit a fast response and a substantially higher sensitivity than existing solid-state sensors at room temperature. Sensor reversibility is achieved by slow recovery under ambient

conditions or by heating to high temperatures. The interactions between molecular species and SWNTs as well as the mechanisms of molecular sensing by nanotube molecular wires are investigated. This last strategy is adopted also in the present study whose purpose is assessment, with quantum mechanical detail, of the adsorbing properties of SWNT. This study is based on DFT and the calculations are applied to a system formed by polychlorinated biphenyl molecules deposited onto a SWNT nanosensor. We discuss the formation mechanisms for them in aqueous solution. The calculations illustrated that SWNT is highly effective in polychlorinated biphenyls removal from the environment. All the calculations were carried out using Gaussian program package.

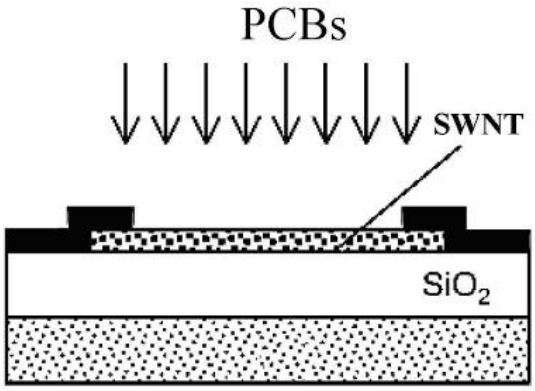

Fig. 1. Cross sectional structure of the SWNT field effect transistors (FET-based sensor) and the experimental geometry[10]

EXPERIMENTAL

The geometry optimizations were performed using an all-electron linear combination of atomic orbital density functional theory (DFT) calculations using Gaussian program package. The optimizations of solids, including exchange and correlation contributions, were carried out using becke's three-parameter hybrid[11-13] and Lee-Yang-Parr (LYP) correlation [B3LYP]; consisting of both local and non-local terms. We have also performed calculations at the B3LYP/6-31G** level of theory with the purpose of obtaining the correlated (LYP) wave function. In addition, calculations of the NMR shifts with the magnetic field perturbation method with gauge in dependent atomic orbital (GIAO) incorporated with this program.

In present research, we report a (B3LYP) density functional study on isotropic ^{13}C and ^{1}H chemical shifts for SWNT using polychlorinated biphenyl. We have used single point geometrics at the gradient-corrected density functional level of theory with 6-31G** quality basis set both for the systems of interest and the standard for calculation of isotropic chemical shifts (TMS).

The isotropy shielding values are defined as follows:

$$\sigma_{iso} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (1)$$

(σ_{ii} being the principal tensor components) were used to calculate the isotropy chemical shifts δ with respect to ($\sigma_{iso} = \sigma_{iso} - \sigma_{aniso}$). Another advantage of these methods for specific and well-parameterized molecular systems, is their capability of calculating values that are closer to experimental observations than those obtained from lower level *ab initio* techniques. The accuracy of semi-empirical quantum mechanics method depends on the database used to parameterize the method. The information obtained from semi-empirical calculations can use to investigate many thermodynamic and kinetic aspects of chemical processes. Energies and geometries of molecules have clear relationships to chemical phenomena. The heat of formation is calculated for these methods by subtracting atomic heats of formation from the binding energy. MNDO has been used widely to calculate heats of formation, molecular geometries, dipole moments, ionization energies, electron affinities and other properties[14,15]. Ball-and-stick models of the SWNT and polychlorinated biphenyl are shown in Figs. 2 and 3. The electronic structure and the conductance properties are calculated for them by DFT.

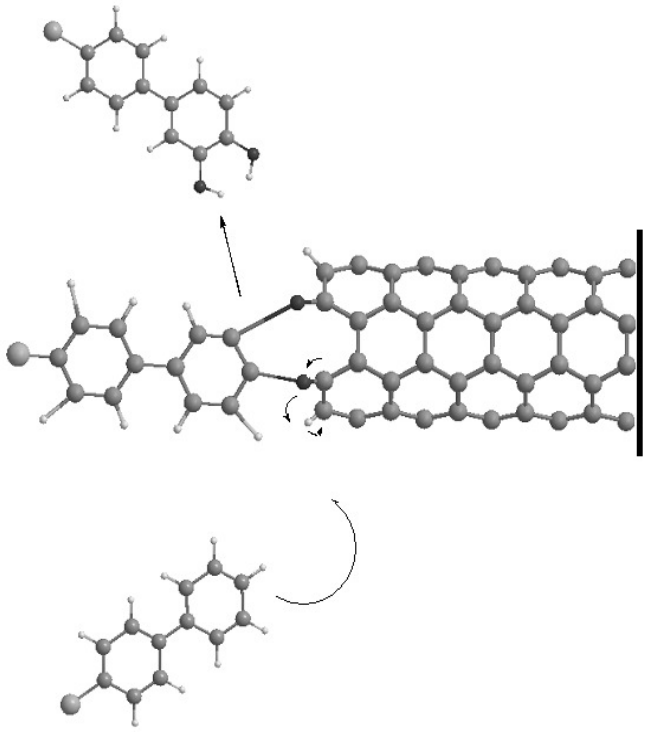

Fig. 2. Simulation of adsorption of polychlorinated biphenyl of surface (SWNT) dihydrodiol so converted 2,3-dihydroxy polychlorinated biphenyl

RESULTS AND DISCUSSION

In many studies, CNT- based sensors have often been fabricated into a thin film configuration rather than into single SWNT, multiple SWNTs and CNT array configurations[16-18]. With well-dispersed CNT solution, CNT thin films could be formed by various techniques such as screen printing[16], spin coating[19], spraying[17], ink-jet printing[18] and imprinting[20]. In this study we calculated the thermodynamic and NMR properties of polychlorinated biphenyl on sensor which was composed of a single-walled carbon nanotube (SWNTs/silane) hybrid thin film deposited by simulation in chemical programs (Figs. 2 and 3).

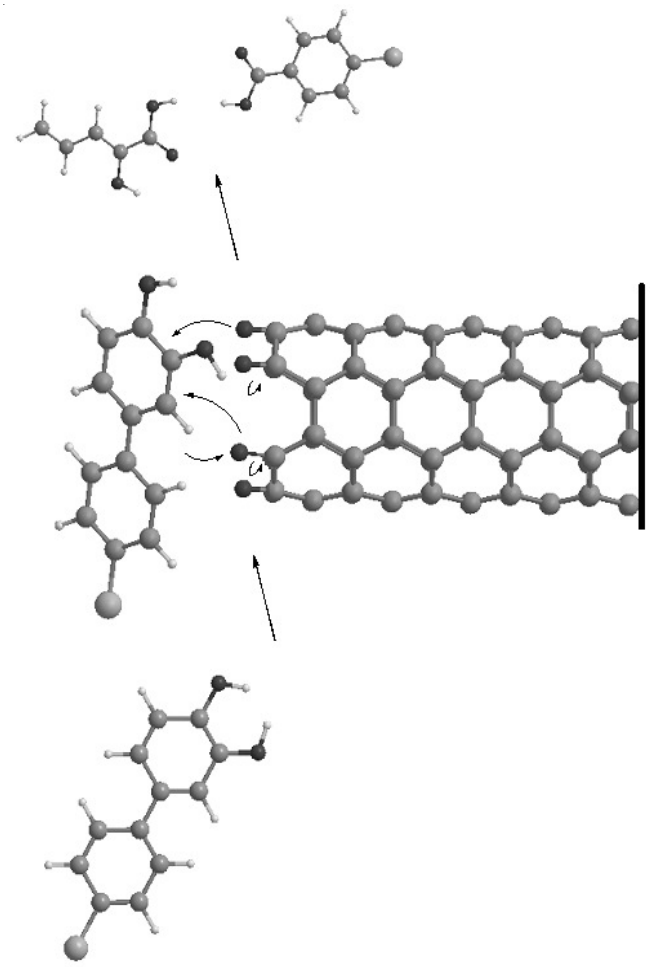

Fig. 3. Simulations of adsorption 2,3-dihydroxy-polychlorinated biphenyl of surface (SWNT) so converted 4-chlorobenzoic acid and 2-hydroxypenta-2,4-dienoic acid.

The sensor was based on the principle that the electronic properties of CNTs change when subjected to strains. The isotropic nature of CNT films helps measure strains in multiple locations and in different directions. This manuscript demonstrated using first-principle quantum transport calculations, semi-empirical with MNDO method that hydrostatic pressure can induce radial deformation and therefore, electrical transition of SWNTs.

Conversion of polychlorinated biphenyl to other products on SWNT: In this work, polychlorinated biphenyl, after getting close to SWNT and in the present O_2, is converted to 2,3-dihydroxy-polychlorinated biphenyl, which is adsorbed on the surface and is later reduced to 4-chlorobenzoic acid and 2-hydroxypenta-2,4-dienoic acid (Fig. 4). All steps were simulated by chemical program package, their geometry optimizations were performed using B3LYP/6-31G** by DFT methods. The mechanism of converting polychlorinated biphenyl to other products on nano-sensor SWNT were calculated using MNDO methods and NMR-DFT, because MNDO calculates heats of formation, molecular geometries, dipole moments, ionization energies, electron affinities and other properties for them.

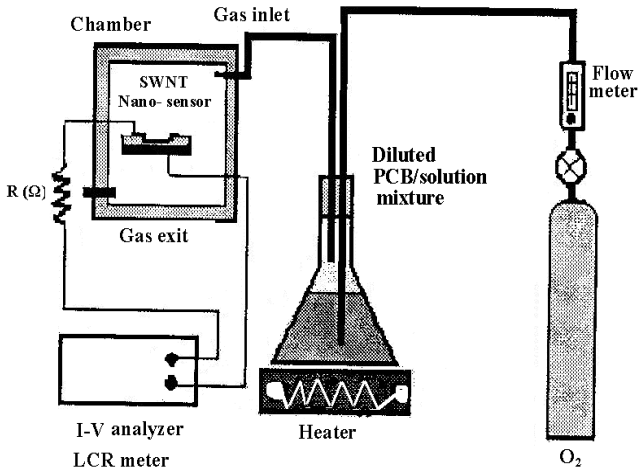

Fig. 4. A set of equipment for testing polychlorinated biphenyl gas sensors[21]

At first, the reaction between the reducing gas and O^- or O^{2-} leads to reduction of the carrier hole density in the surface charge layer and the decrease of the electric resistance of SWNT. The oxygen molecule is neared to the SWNT; then it is converted to oxygen atom or molecules of ion absorption on surface (Fig. 5). The semi-conductivity in SWNT must be due to large oxygen deficiency in it. The material would then adsorb the oxygen species at higher temperatures ($O_2^- \rightarrow 2O^- \rightarrow O^{2-}$).

TABLE-1
THERMODYNAMIC PROPERTIES OF POLYCHLORINATED BIPHENYL CONVERTED TO OTHER PRODUCTS ON SWNT-NANO SENSOR

Distance (A°)	E_{total} (MJ/mol)	RMSD	Dipole moment (D)	E_{nuc} (MJ/mol)	G_{ele} (MJ/mol)	H (MJ/mol)	E_{bin} (MJ/mol)	E_{ele} (v)
Polychlorinated biphenyl converted to 2,3-dihydroxy-polychlorinated biphenyl								
6.87	-10407.75	1.67×10^{-5}	8386	19052.20	-13790.47	6977.94	6909.32	-142.91
3.64	-10407.69	1.58×10^{-5}	8604	19172.93	-14325.54	6563.60	6494.98	-148.45
2.72	-10404.61	1.52×10^{-5}	8556	19244.52	-14415.85	6541.08	6472.90	-149.39
6.23	-10405.24	1.43×10^{-4}	8770	19022.41	-14308.82	6425.92	6357.81	-148.28
2,3-dihydroxy-polychlorinated biphenyl converted to 4-chlorobenzoic acid and 2-hydroxypenta-2,4-dienoic acid								
7.32	-10785.27	1.36×10^{-5}	8770	-22152.85	-156.58	-225.26	4806679	-229.56
3.45	-10785.28	2.29×10^{-5}	8975	-14687.35	7494.03	7425.34	4850752	-152.20
2.75	-10785.22	2.81×10^{-6}	9421	-22436.88	-157.19	-225.87	4874159	-232.51
2.65	-10787.68	4.10×10^{-5}	9506	-15367.12	6718.63	6649.50	4827076	-159.25
2.98	-10983.29	8.05×10^{-6}	9742	-22133.32	-160.56	-230.37	4787863	-229.36
6.75	-10983.29	4.33×10^{-6}	9742	-14169.78	7358.28	7288.47	4681982	-146.84

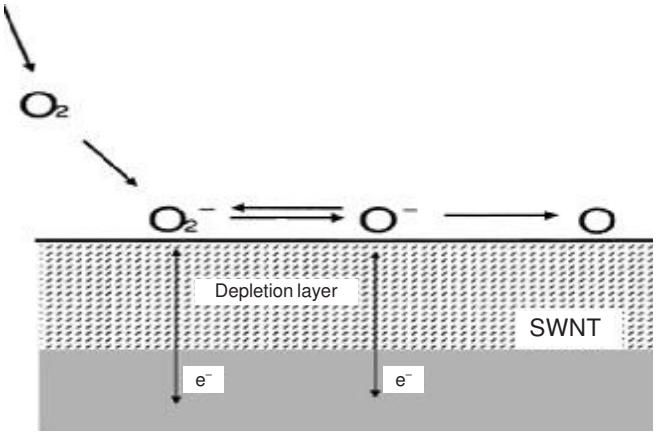

Fig. 5. The interaction of O_2 on the SWNT

The thermodynamic properties of polychlorinated biphenyl conversion into 2,3-dihydroxy-polychlorinated biphenyl, 4-chlorobenzoic acid, 2-hydroxypenta-2,4-dienoic acid is showed Table-1. The total energy (MJ/mol) of polychlorinated biphenyl convertion to 2,3-dihydroxy-polychlorinated biphenyl is increasing and this is an exothermic reaction, but E_{total} for product of 4-chlorobenzoic acid and 2-hydroxypenta-2,4-dienoic acid is decreasing (Fig. 6), therefore, dipole moment (D) is enhanced for them since there are OH and COOH for binding them.

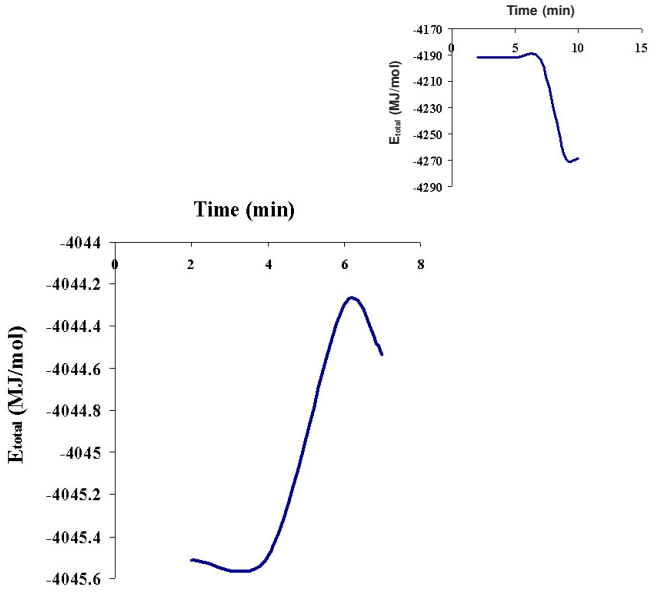

Fig. 6. The total energy (MJ/mol) of conversion polychlorinated biphenyl to: (a); 2, 3-dihydroxy-polychlorinated biphenyl and (b); 4-chlorobenzoic acid and 2-hydroxypenta-2,4-dienoic acid

The binding energies are calculated as follows: E_{bin} = E(tube + polychlorinated biphenyl) - E(tube) - E(polychlorinated biphenyl), where E(Tube + polychlorinated biphenyl) is the total energy for the system tube + polychlorinated biphenyl, E(tube) is the total energy for the pure SWNT and E(polychlorinated biphenyl) is the energy of an isolated polychlorinated biphenyl atom in the ground state conjugation.

The adsorption rate, electric and binding nuclear energy, RMS gradient, heat of formation and Gibbs free energy are calculated through MNDO methods in semi-empirical quantum in DFT and the electric resistance for them is as follows:

$$E_{elec} = RI \quad (2)$$

where, E_{elec} is electric energy (V), R(Ω) is electric resistance, I (A) is electric intensity that is $I = \frac{q}{t}, q(C)$ is electric charge and t is time interaction, which is in following form in experimental data:

$$R = \frac{E_{elec} t}{nF} \quad (3)$$

where n, F and t are electron number of conversion, faraday constant and time (h), respectively. R (Ω) is reduced for those shown in Fig. 7. The calculated magnetic shielding in Tables 2 and 3 was converted into σ_{iso}, σ_{anso} chemical shifts by ^{13}C absolute shielding in SWNT at the same level of theory. It is worth noting that the last approach leads to a substantial improvement in the calculated magnetic properties. Calculations of the NMR shifts through the magnetic field perturbation method of GIAO (gauge in dependent atomic orbital) were incorporated.

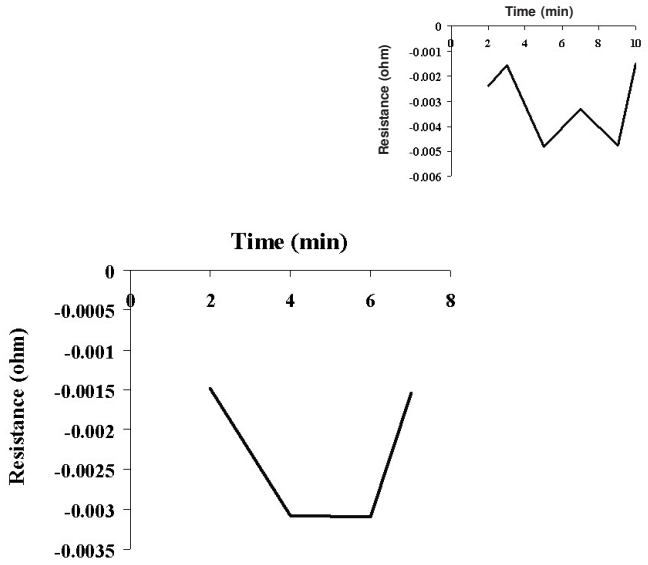

Fig. 7. The electric resistance (O) of conversion polychlorinated biphenyl to: (a); 2, 3-dihydroxy-polychlorinated biphenyl and (b); 4-chlorobenzoic acid and 2-hydroxypenta-2,4-dienoic acid

The results of calculations for O atoms adsorption to SWNT (Fig. 8, part a) and for adsorption of Cl atoms of polychlorinated biphenyl in vicinity of SWNT (Fig. 8, part b) have been shown in Tables 2 and 3. In these calculations, in addition to the aforementioned atoms, some other atoms from SWNT, polychlorinated biphenyl and 2, 3-dihydroxy-polychlorinated biphenyl (Fig. 8) have been studied by NMR-DFT methods. Regarding the method for achievement of gauge invariance for the present case, at the B3LYP level on GIAO is found to be slightly superior.

The O atoms adsorbed on the SWNT in this interaction have most changing σ_{iso}, σ_{aniso} chemical shifts. σ_{iso} for O_{81} and O_{82} is increased by 3.67 and 6.23 nm, because polychlorinated biphenyl converted to 2,3-dihydroxy-polychlorinated biphenyl

TABLE-2
NMR ISOTROPY AND ANISOTROPY FOR POLYCHLORINATED BIPHENYL to
2,3-DIHYDROXY- POLYCHLORINATED BIPHENYL by B3 LYP/6-31G** METHOD

Distance (A°)	O_{81}		O_{82}		C_{84}		C_{85}		Cl_{100}	
	Isotropy	Anisotropy	Isotropy	Anisotropy	Isotropy	Anisotropy	Isotropy	Anisotropy	Isotropy	Anisotropy
6.87	1328.45	-980.54	8304.73	933.52	167.59	123.45	164.99	103.21	67.83	1041.33
3.64	4497.19	-1182.6	47754.40	6219.40	250.44	129.57	239.47	101.03	218.40	980.61
2.72	1794.90	-210.08	6939.03	544.39	157.61	132.92	805.88	-385.90	63.44	1043.95
6.23	6524.53	-4020.40	10623.23	-653.80	122.32	150.46	155.04	107.71	62.96	1043.12

TABLE-3
NMR ISOTROPY AND ANISOTROPY FOR 2,3-DIHYDROXY-POLYCHLORINATED BIPHENYL TO
4-CHLOROBENZOIC ACID AND 2-HYDROXYPENTA-2,4-DIENOIC ACID BY B3 LYP/6-31G** METHOD

Distance (A°)	O_{81}		O_{82}		O_{103}		O_{105}	
	Isotropy	Anisotropy	Isotropy	Anisotropy	Isotropy	Anisotropy	Isotropy	Anisotropy
7.32	-6804.87	396.59	76020.00	8911.27	27759.00	-7887.20	21623.30	5438.58
3.45	565.67	82.61	4999.00	-2987.32	21713.90	-4917.30	11313.60	1038.48
2.75	-1374.60	-184.48	16637.00	1253.86	118813	-21361.00	4130.29	1088.43
2.65	-489.17	-325.50	211.1	331.54	104.88	361.27	1056.46	1076.36
2.98	-121.92	-158.57	109.9	266.72	65.86	337.18	892.17	917.13
6.75	-132.56	-151.46	110.2	264.80	62.33	337.74	904.99	906.73
Distance (A°)	O_{80}		O_{84}		O_{85}		O_{100}	
	Isotropy	Anisotropy	Isotropy	Anisotropy	Isotropy	Anisotropy	Isotropy	Anisotropy
7.32	1174.34	318.34	211.35	163.05	529.41	70.23	80.81	1048.92
3.45	125.70	15.16	181.99	139.85	186.62	72.12	47.19	1070.13
2.75	449.32	156.48	693.04	24.44	266.32	115.52	171.40	1113.36
2.65	93.66	109.36	270.27	52.22	109.54	109.24	44.99	1056.68
2.98	101.08	102.20	100.56	101.93	109.05	122.31	137.44	986.82
6.75	102.49	99.19	101.45	101.34	106.12	122.81	138.67	986.14

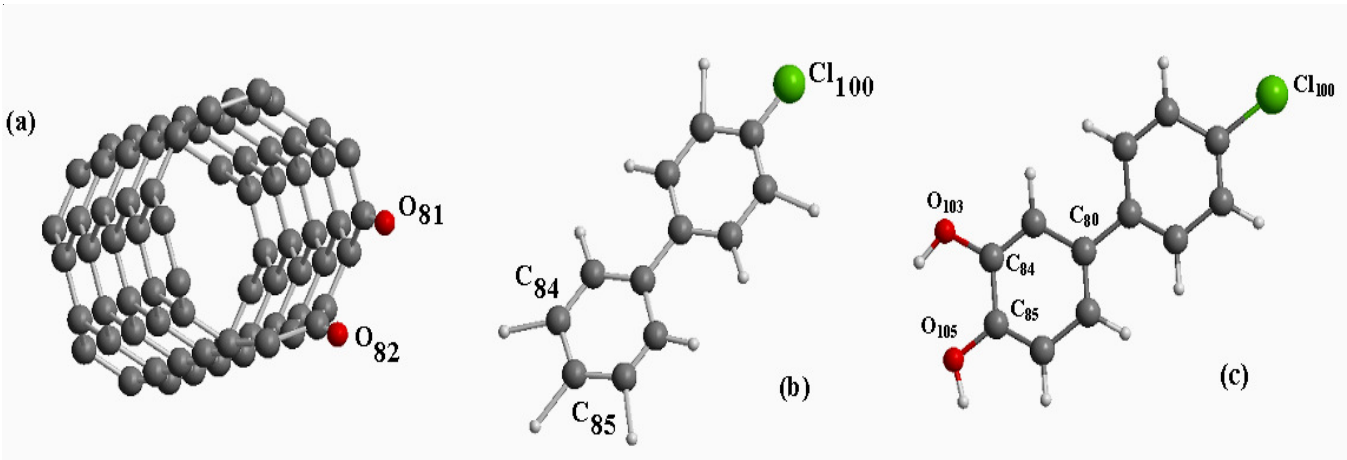

Fig. 8. Atoms numbers are investigated by magnetic shielding NMR-DFT: (a) SWNT, (b) PCB, (c) 2,3-dihydroxy-PCB in all spaces

at last. The NMR data for conversion of 2,3-dihydroxy-polychlorinated biphenyl to 4-chlorobenzoic acid and 2-hydroxypenta-2,4-dienoic acid is shown in Table-3. In this interaction, there are some 2,3-dihydroxy-polychlorinated biphenyl near O atoms on SWNT, which are attracted on them to be converted to other products. σ_{iso}, σ_{anso} chemical shifts differs for O atoms and C_{80} atom of this interaction are a lot but other atoms have most changing in 2.75 nm only.

Conclusion

Polychlorinated biphenyls have been widely used in flame-retard products common in homes and workplaces and they have subsequently become widely dispersed in the environment. Polychlorinated biphenyls are widespread toxic pollutants and are recently being scrutinized for potential environment damage in groundwater and in the atmosphere.

For removing polychlorinated biphenyls from the environment, we suggest using SWNT, which is a good environmental pollution nanosensor. The SWNTs able to extract polychlorinated biphenyl and to convert it to other products.

For describing the simulation and calculation of polychlorinated biphenyl removal by SWNT, we disregard the other environment interactions. We choose armchair single walled-carbon nanotube (4, 4) and passing polychlorinated biphenyl through it is investigated and the interaction between them is calculated by *ab initio*. A change in the potential of all atoms on SWNT surface is observed for polychlorinated biphenyl.

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