



Research Paper

Theoretical Assessment of Static and Dynamic Polarizabilities of Single-Walled Carbon Nanotubes: Semi-Empirical PM6 Study

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ABSTRACT

Armchair carbon nanotubes (n,n) with n = 5, 6, 7, 9 and 10 saturated with hydrogen at the ends was studied using semi-empirical PM6 methods. Our results allowed sorting out the considered CNTs by decreasing molecular polarizability value. To understand this phenomenon in the context of molecular orbital picture, the molecular HOMOs and molecular LUMOs energies were examined. An excellent agreement between the PM6 polarizability value and the number of carbon atoms in armchair-CNTs gave a correlation coefficient of 0.99. The study revealed that the Armchair carbon nanotubes had large polarizabilities values and hence, may have potential applications in the development of non linear optical materials.

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INTRODUCTION

Due to their unique structures and excellent electrical and optical properties, especially their unparalleled thermal and mechanical stability, CNTs have long been proposed as novel nanomaterials in a wide variety of applications including composite materials (Luo et al., 2008; Guo et al., 2004), molecular sensing (Chen et al., 2009; Castro et al., 2009), energy conversion and energy storage (Arranz-Andres and Blau, 2008; Hino et al., 2006) and nanoelectronic devices (Curran et al., 2009).

Interestingly, a large effort is put into understanding the optical response properties of the materials and specifically the molecular polarizabilities which help the construction of new optoelectronic and photonic devices (Karna, 2000; Kanis et al., 1994). Similar to polyenes, CNTs nanosystems with their extensive delocalized π -electron systems emerged as potential candidates for non-linear optical applications. Recently, For nano-sized systems, quantum chemical methods have profoundly changed the science of designing, developing and interpreting structure-property relationships of NLO molecular materials. Experimentalists are able to apply chemical intuition in concert with the insight provided by such contemporary computations to effectively guide synthetic strategies (Afshan et al., 2011; Muhammad et al., 2009, 2010).

Non-linear optical (NLO) materials are the smartest materials with the ability to generate new electromagnetic fields with changed frequencies, phases and other physical properties. In view of their intriguing structural and electrical properties, the linear and non-linear optical (NLO) responses of carbon Nanotube (CNT) molecules have been explored by using molecular modelling methods. To the best of our knowledge, no studies of the polarizability of finite CNTs have been carried out using semi-empirical PM6 methods. Hence, in this work the mean static and dynamic polarizabilities and polarizabilities tensor components for CNTs at the PM6 levels were calculated.

COMPUTATIONAL DETAILS

The geometry of tubular armchair CNTs structures composed by carbon containing from 100 to 200 atoms with saturated hydrogen atoms at tube ends were fully optimized through the MM + force field using HyperChem v8 (Molecular Modelling System, 2000). Static and dynamic polarizabilities were evaluated by the semi-empirical quantum chemical method Parametric Method 6 (PM6) (Stewart, 2012).

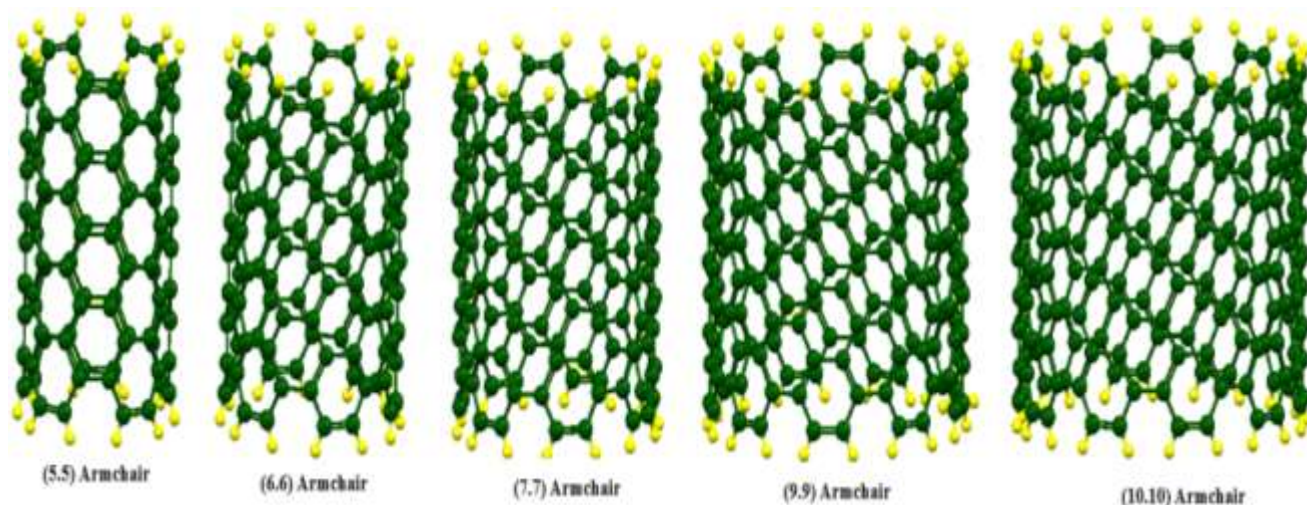


Figure 1: Optimized armchair nanotubes studied: (5.5); (6.6); (7.7); (9.9) and (10.10).

Table 1: Total energy and energy per carbon atom with varying diameters for Armchair- CNTs.

Armchair nanotubes	Nombre of carbon atoms N_c	E_{TOT} (Kcal/mol)	E/N_c (Kcal/atom)	Tube diameter (Å)
(5.5)	100	536.001	5.360	6.78
(6.6)	120	443.978	3.700	8.11
(7.7)	140	366.853	2.620	9.47
(9.9)	180	250.444	1.391	12.21
(10.10)	200	201.819	1.009	13.57

PM6 is a semi-empirical method derived from the Hartree-Fock theory. The advantages of semi-empirical calculations are that they are much faster than DFT and ab initio calculations and can be used for large organic molecules.

RESULTS AND DISCUSSION

Structural properties and total energy

Figure 1 shows the geometries of the Armchair carbon nanotubes considered in the present study. This corresponds to the optimized conformations of tubes (5.5), (6.6), (7.7), (9.9) and (10.10) which have diameters from 6 to 13 Å.

As can be observed in optimized structures nanotube molecules do not show irregularities along the tube walls. At the same time, the evolution of the total energy as a function of the total number of carbon atoms E/N_c (Kcal/atom) increases with small nanotubes diameters. We conclude that stressed small diameter nanotubes are less stable than the wider tubes (Table 1). Large diameter tubes are preferred for nanoelectronics since they form good contact with the electrodes and can carry high current (Kim et al., 2005).

Electronic structure of Armchair- CNTs

In Figures 2 and 3, we plot the HOMO–LUMO energy and E_{gap} versus the number of atoms, respectively. It can be seen that the gap strongly depends on the number of atoms and tube diameter. As the tube diameter increases, the HOMO–LUMO gap decreases. The E_{gap} of this systems show a decreasing trend with increasing tube diameter and approaches the lowest value in (10.10) armchair CNTs.

The relation between E_{gap} and tube length in infinite Armchair-CNT capped with either hydrogen atoms were also examined. Figure 4 shows an oscillation of the gap with increasing length of the tube, the HOMO-LUMO gap of armchair (3,3) tubes decrease as the length of the tube increases.

Polarizabilities

The static dipole polarizability is a measure of the distortion of the electronic density and the information about the response of the system under the effect of an external static electric field. The results of static and dynamic polarizability (α) and polarizabilities tensor components using semi-empirical PM6 for armchair- CNTs tubes (Figure 1) are given in Table 2.

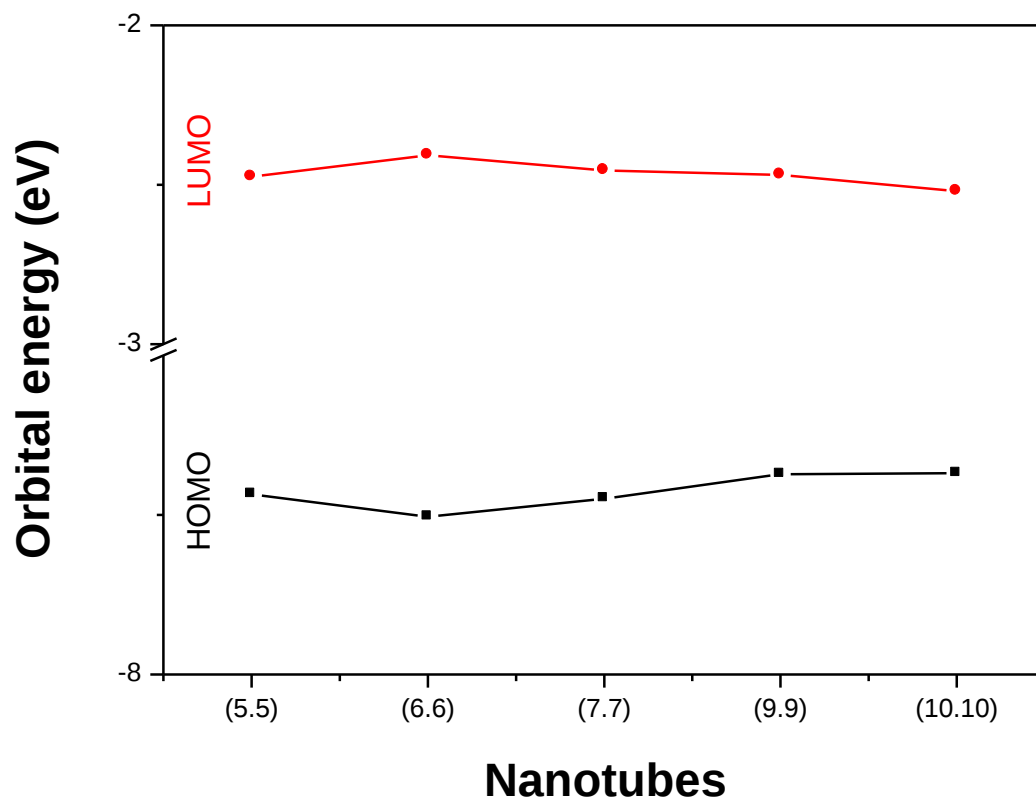


Figure 2: The HOMO and LUMO energy vs the number of carbon atoms that comprise the tube.

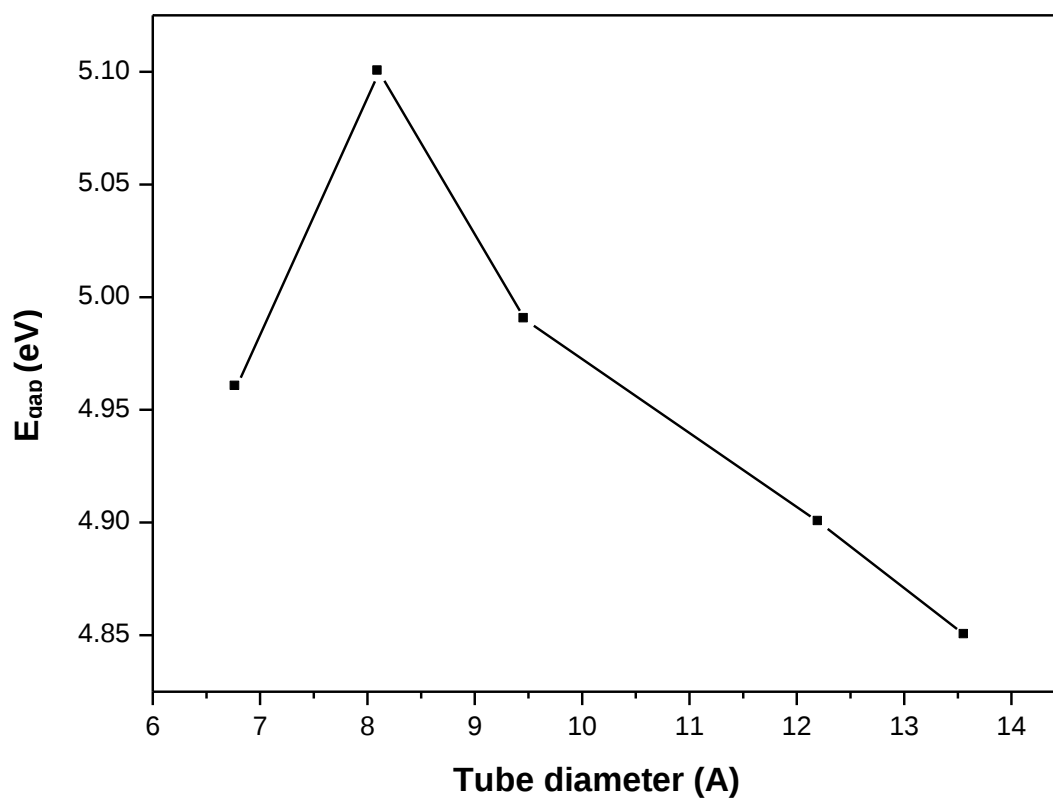


Figure 3: Dependence of E_{gap} of Armchair-CNT on the tube diameter.

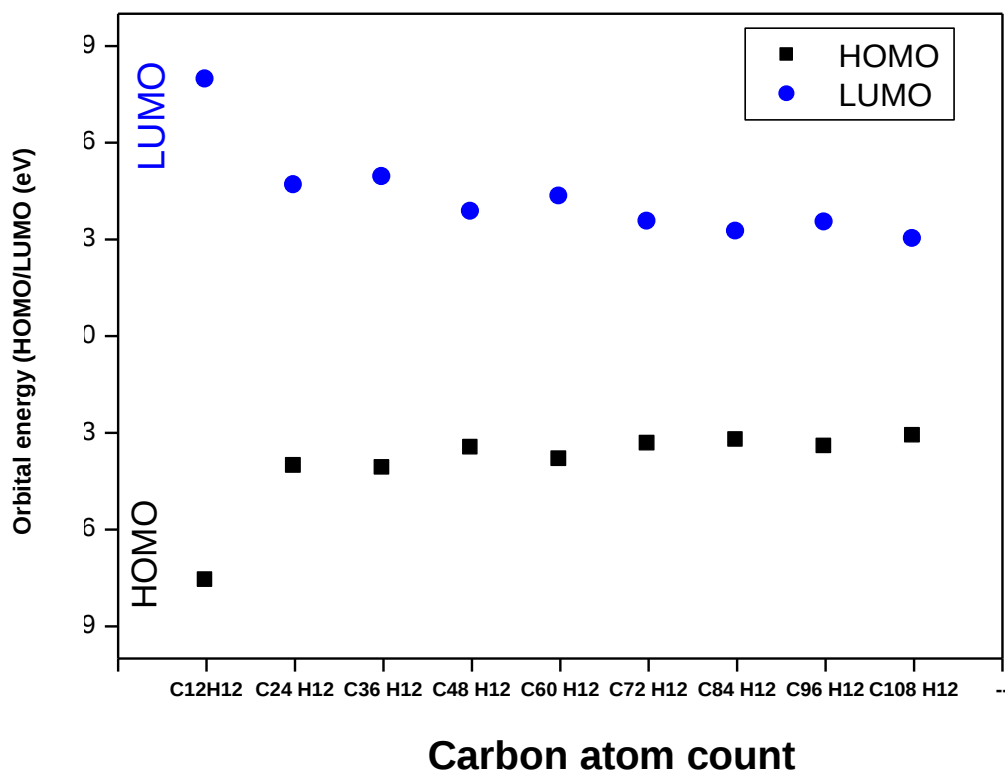


Figure 4: Energy of HOMO and LUMO vs. The number of C atoms in (3,3) CNTs.

Table 2: Static and dynamic polarizabilities, polarizability polarizability components and number of carbon atoms N_c . The α values are given in atomic units. $1.0 \text{ a.u. of polarizability} = 1.6488 \times 10^{-41} \text{ C}^2 \text{ m}^2 \text{ J}^{-1} = 0.14818 \text{ \AA}^3$.

Nanotubes	Numbre of carbon atoms N_c	$\omega = 0$			
		α_{xx}	α_{yy}	α_{zz}	$\langle \alpha \rangle$
(5.5)	100	1490.45	956.09	955.02	1133.86
(6.6)	120	1764.71	1223.64	1223.57	1403.97
(7.7)	140	2042.04	1514.77	1514.54	1690.45
(9.9)	180	2177.36	2133.21	2611.25	2307.28
(10.10)	200	2506.86	2505.06	2890.53	2634.15

Nanotubes	Number of carbon atoms N_c	$\omega = 1239.84 \text{ nm}$			
		α_{xx}	α_{yy}	α_{zz}	$\langle \alpha \rangle$
(5.5)	100	1563.84	982.95	981.85	1176.22
(6.6)	120	1846.30	1265.81	1265.74	1459.28
(7.7)	140	2132.83	1580.64	1580.38	1764.61
(9.9)	180	2355.12	2601.46	2738.27	2564.95
(10.10)	200	2790.03	2787.30	3013.60	2863.64

The mean polarizability was calculated from the polarizability components as (Kanis et al., 1994):

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (1)$$

Table 2 compares the calculated values of static and dynamic polarizabilities for all- Armchair- CNTs. For all series, the dynamic polarizabilities are slightly higher than the static and the percent difference is about 1%. From compounds under study, the smallest and the largest enhancement of average static and dynamic polarizabilities are due to the (9.9) and (10.10) Armchair- CNTs

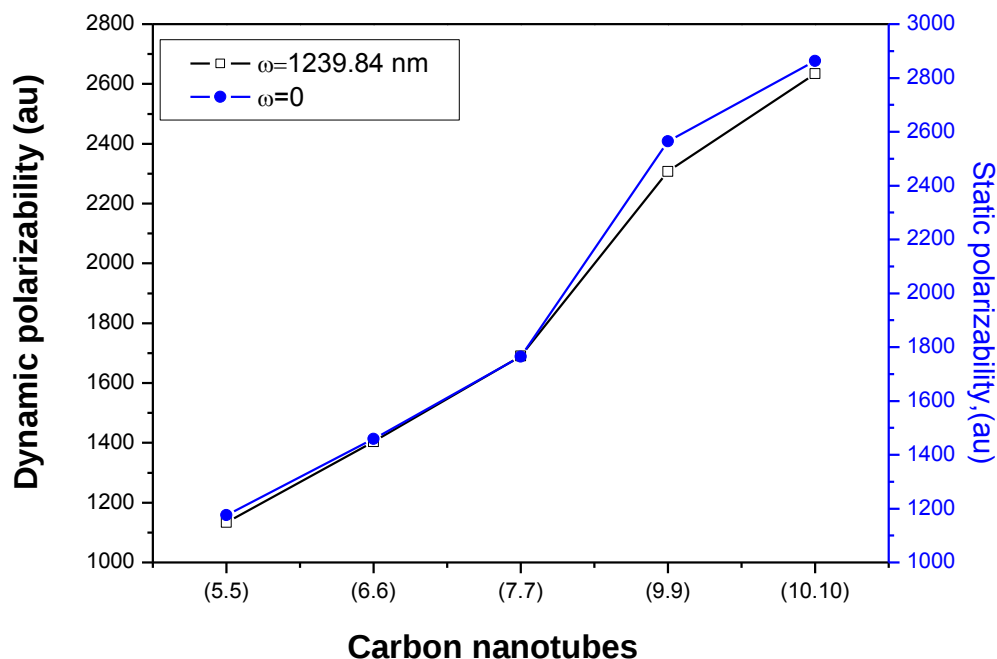


Figure 5: Static and dynamic polarizabilities of armchair-CNTs.

respectively. For both static ($\omega = 0$) and dynamic ($\omega = 1239.84$ nm) case, the polarizabilities are dominated by the longitudinal component α_L , which means a preferential orientation of the polarizability along α_{xx} axis. However, the axial components polarizabilities, α_{yy} and α_{zz} show a similar variation trend and their values are commonly low in relation to the longitudinal component α_{xx} .

The results (Figure 5) also show a good proportionality between the average polarizability values and the number of carbon atoms N_c in nanotubes. For both static and dynamic polarizabilities, the largest increment of α is seen to be due to the larger tube diameter. As regards to the tube diameter of armchair-CNTs, we are able to propose a decreasing classification, relatively to the mean polarizability $\langle \alpha \rangle$. The established order is as follows: $\alpha(10.10) > \alpha(9.9) > \alpha(7.7) > \alpha(6.6) > \alpha(5.5)$.

Since calculating polarizability of large nanostructures by PM6 techniques requires high computational load, a correlation between the structure and mean polarizability was sought. Figure 6 shows the graphical representations of static and dynamic mean polarizabilities versus the number of number of carbon atoms in Armchair-CNTs. We found that the mean polarizabilities calculated by PM6 methods are linearly correlated with the number of carbon atoms in Armchair-CNTs. Based on this fact, one can extrapolate $\langle \alpha \rangle$ for infinite Armchair carbon nanotubes (n,n) .

Static polarizability: ($\omega = 0$) given as:

$$\langle \alpha \rangle^{\text{PM6}} = -393.55953 + 15.05069 N_c \quad (R^2 = 0.999) \quad (1)$$

Dynamic polarizability: ($\omega = 1239.84$ nm) given as:

$$\langle \alpha \rangle^{\text{PM6}} = -606.02674 + 17.3768 N_c \quad (R^2 = 0.998) \quad (2)$$

Bond length alternation

The works of Marderv and Perry (1993) investigated on the basis of semi-empirical calculations, relations between structure and polarizabilities in π -conjugated polyenes compounds showed that the NLO responses of these systems can be optimized by varying the geometric parameter defined as bond length alternation (BLA).

Table 3 shows that large carbon nanotube diameter make greater structural changes as compared to the small ones. As the tube becomes wider, the two bond lengths approach each other. Increasing the diameter of the nanotubes (CNTs) led to an increase of bonding energy E_{Bond} and the decrease in steric energy which in turn result in an approximation of the lengths of two C-C bonds. As a consequence, the ratio $d_{\text{diag}}/d_{\text{perp}}$ decrease from nanotubes (5.5) to (10.10) by 2%. The bond length alternation ($\text{BLA} = (d_{\text{diag}} - d_{\text{perp}})$) decreases when going from nanotubes (5.5) to (10.10). A decreasing ranging from 0.189 and 0.161 Å is observed.

The semi empirical PM6 methods shows that mean static and dynamic polarizabilities decreases upon decreasing the BLA. When going from $\text{BLA} = 0.189$ Å for nanotubes (5.5) to $\text{BLA} = 0.161$ Å for (10.10) tubes, the molecular polarizabilities $\langle \alpha \rangle$ decreases by factors of approximately 3. This means that, the smaller the BLA, the smaller the $\langle \alpha \rangle$ values. Based on the previous discussions on the link between the BLA and polarizability $\langle \alpha \rangle$, the two sets of quantities were plotted in Figure 7. A correlation between

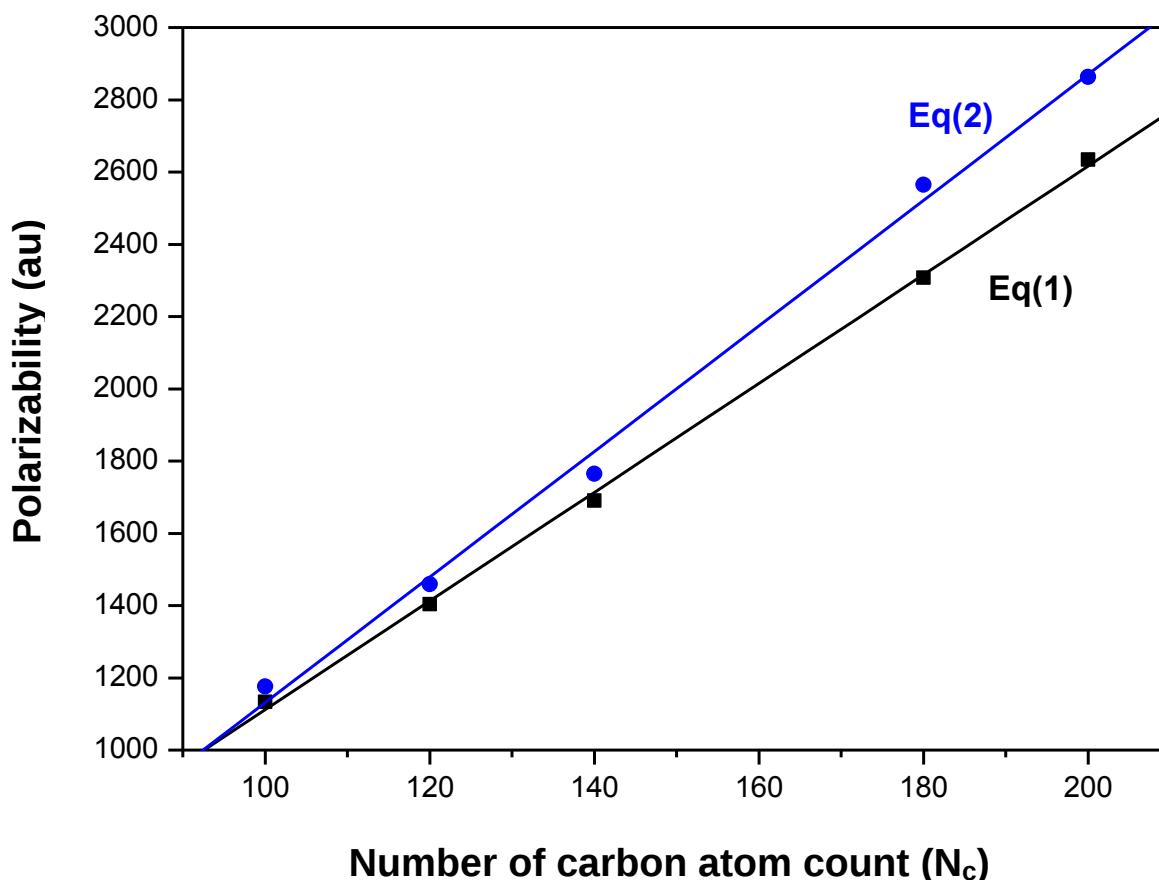


Figure 6: Correlation between the static and dynamic polarizability of Armchair-CNTs and the number of carbon atoms.

Table 3: Bonding energy and lengths of the C-C bonds diagonal and perpendicular to the tube axis in armchair-CNTs with tube diameters.

Nanotubes	$d_{\text{perp}}/\text{\AA}$	$d_{\text{diag}}/\text{\AA}$	$d_{\text{diag}}/d_{\text{perp}}$	E Bond (KJ/mol)	BLA = ($d_{\text{diag}} - d_{\text{perp}}$)
(5.5)	1.316	1.505	1.144	0.34	0.189
(6.6)	1.319	1.498	1.136	11.27	0.179
(7.7)	1.322	1.492	1.129	12.79	0.170
(9.9)	1.324	1.489	1.125	15.70	0.165
(10.10)	1.325	1.486	1.122	17.05	0.161

the polarizability and the BLA was found. The corresponding linear correlation coefficient is found to be 0.94, indicating the reliability of the correlation. This is an important observation that can provide a way to calculate the polarizability of the larger tubes from the values of BLA.

Conclusions

In the present work, mean polarizabilities of the armchair carbon nanotubes (n,n) with $n = 5, 6, 7, 9$ and 10 saturated with hydrogen at the ends was studied by the semi empirical PM6 methods. It is evident that polarizability

tensor of carbon nanotubes strongly depends on their electronic structure. The HOMO-LUMO gap is found to decrease with increase of tube diameter whereas it decreases as the length of the tube increases.

Mean static and dynamic polarizabilities of the armchair carbon nanotubes (CNTs) decreases upon decreasing the bond length alternation (BLA) values. A good proportionality between the average polarizability values and the number of carbon atoms N_c in nanotubes was obtained. General linear correlation between the static and dynamic polarizability and the number of carbon atoms was obtained. It can be used for the prediction of polarizabilities of larger CNTs tubes without demanding

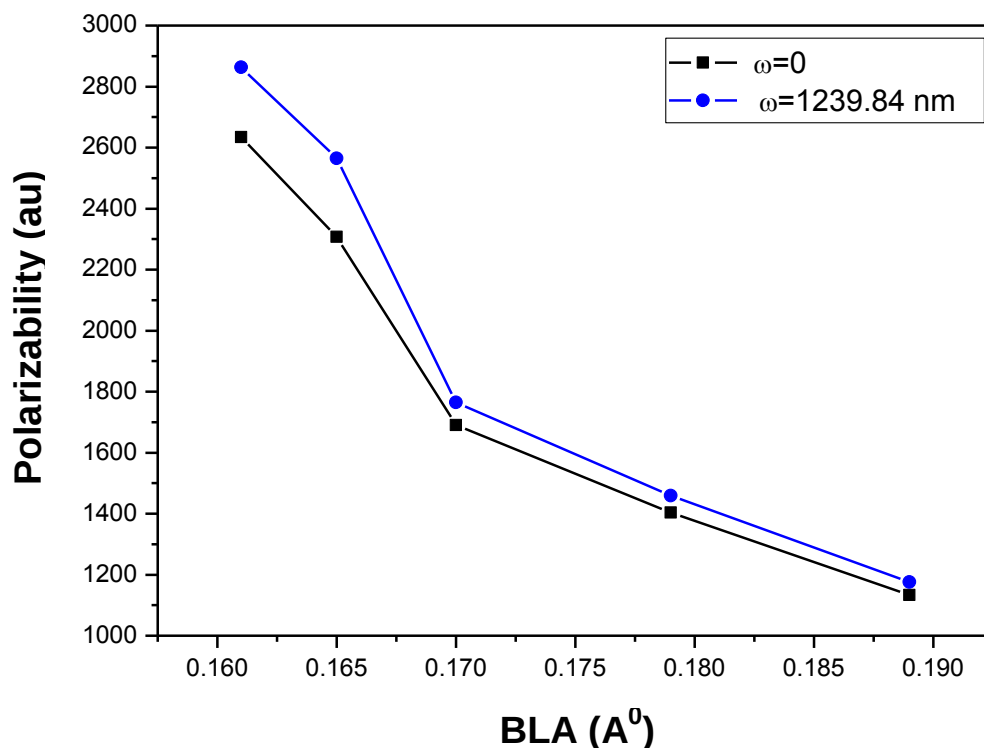


Figure 7: The mean polarizabilities for CNTs as function of the BLA ($\text{\AA}$).

therotical calculations.

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